General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.

- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.

- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.

- This document is paginated as submitted by the original source.

- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

Produced by the NASA Center for Aerospace Information (CASI)

NASA CR-
147780

Mechanisms of Deterioration of Nutrients

by

Marcus Karel and James M. Flink

Department of Nutrition and Food Science
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

ANNUAL REPORT - PHASE IV

NASA/JSC CONTRACT No. 9-12485

(NASA-CR-147780) MECHANISMS OF DETERIORATION OF NUTRIENTS ANNUAL REPORT, 13 MAR. 1975 - 13 MAR. 1976 (MASSACHUSETTS INST. OF TECH.) 197 P HC $7.50 CSCL 06H
N76-25797
UNCLAS
G3/54 42197

Mechanisms of Deterioration of Nutrients

by

Marcus Karel and James M. Flink

Department of Nutrition and Food Science
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

ANNUAL REPORT - PHASE IV
13 March 1975 - 13 March 1976
NASA/JSC Contract No. 9-12485

Table of Contents

Tables and/or Figures for each section are found at the end of their respective sections.

1. General Introduction

Phase IV of this contract has been devoted to continuation of studies to develop methods by which freeze dried foods of improved quality will be produced. Storage stability of freeze dried fruit products of improved quality, produced according to technology developed in earlier phases of this contract was evaluated. These studies are continuing. Artificial Food Matrices which simulate fruit texture have been developed. These high quality items which can be frozen or freeze dried without loss of the desirable organoleptic properties, are incorporated into various food products.

In particular, studies have continued in the following areas, each of which is covered in a separate section of this Annual Report.

Section 2: Microstructure of Freeze Dried Systems

Microscopic techniques have been refined for use in studying the structure of freeze dried multiphase systems. These optical and electron microscope techniques have been used in conjunction with differential extraction procedures to quantitatively determine the degree to which lipid has segregated between surface coating and matrix encapsulation following freeze drying of emulsified systems. The effect of various process variables on the structure of the freeze dried emulsion has been investigated.

Section 3: Investigation of Structural Changes in Freeze Dried Systems

Many product quality factors depend, either directly or indirectly, on the maintenance of the structure of the freeze dried

materials. This is true both during the freeze drying process and in the storage period which follows. The influence of variation of a number of process conditions on the structure of freeze dried materials has been investigated and is reported in a technical article "Loss of Structure in Freeze Dried Carbohydrate Solutions: Effect of Temperature, Moisture Content and Composition".

Section 4: Artificial Food Matrices (AFM)

Fruit-simulating Artificial Food Matrices have been prepared by a two-step gelation process. The AFM may be flavored as desired. Their desirable texture is stable to freeze/thaw and freeze drying/rehydration cycle. Methods for incorporation of a lipid-soluble and water-soluble vitamin have been investigated. A significant fraction of the recommended daily allowance (USRDA) of vitamin A and vitamin C can be incorporated into the matrix. The rheo-mechanical properties of various combinations of the components of the AFM at a number of process steps have been investigated to aid in elucidation of the factors affecting the interaction of gel materials. Some texture characteristics of representative fruits and vegetables have been measured.

Section 5: Osmotic Preconcentration To Yield Improved Quality Freeze Dried Fruits

Freeze Dried Fruit Slices having improved quality can be prepared by concentrating the fruit prior to freeze drying and by use of a slow freezing process. To achieve the concentration step

the fruit slices undergo an osmosis treatment through immersion in a concentrated aqueous solution. The effect of osmosis process conditions on the extent and rate of osmotic preconcentration of apple slices has been investigated. Solutes which may be substituted for sucrose in the osmosis solution have been tested for their effect on osmosis kinetics.

Section 6: Storage Stability of Osmotically Preconcentrated Freeze Dried Fruits

Freeze Dried Apple Slices which had been prepared using osmotic preconcentration steps with either sucrose or maltodextrin were held in long term storage under a variety of test conditions. The test variables included, osmosis preconcentration solute, storage time, container headspace atmosphere (air vs. vacuum), storage temperature, and sample moisture content (or water activity).

A Summary of the results of Phase IV is presented as Section 7.

2. Microstructure of Freeze Dried Systems

2.1 Introduction

Studies on the microstructure of freeze dried oil-in-water emulsions containing dispersed or dissolved solids have been continued. The location of the lipid phase in the freeze dried matrix was investigated using optical microscopy (OM), scanning electron microscopy (SEM) and electron microprobe analyses (EMP). The distribution of lipid with respect to the matrix (surface ("free") vs. encapsulated) was quantitized by extraction methods developed in Phase IV of this study, namely a hexane extraction at controlled temperature in a soxhlet apparatus for surface oil, followed by an extraction with water, chloroform, and ethanol for determination of encapsulated oil. A separate determination of total oil was obtained by conducting a water-chloroform-ethanol extraction of the initial freeze dried emulsion.

2.2 Development and Refinement of Microscopic Techniques

2.2.1 Techniques Developed

The o/w emulsions contained either triolein or linoleic acid as the lipid phase. Maltodextrin was usually used for the structure forming solute, though in a few cases the effect of incorporating other solutes was examined.

The presence of lipid encapsulated in the matrix of the freeze dried system can be easily observed in the optical microscope. In maltodextrin-based systems the lipid appears as liquid

inclusions with diameters ranging from 1 micron or less to 4-5 microns, depending on concentrations and freezing rate.. Occasionally, air inclusions and holes can also be seen. The portion of the total sample oil which is not encapsulated can be determined in the optical microscope only after reaction of the unsaturated bonds of the lipid with osmic acid (OsO_4) vapors. By exposing a freeze dried sample to OsO_4 vapors, the surface fat becomes visible as dark brown or black areas on the surface.

A number of electron microscopic techniques have been evaluated for their ability to detect surface fat in freeze dried emulsions. Heavy metals (ferrocene and tetraethyl) lead were incorporated in the oil phase by dissolving in organic solvents. After freeze drying, the samples were viewed in the SEM using three methods of image formation:

a) Secondary electron (the standard SEM operating mode)

b) Backscatter (mode which selectively detects higher energy backscattered electrons which come from higher atomic weight targets)

c) Absorption Current (mode which images by variation of current as it is being scanned over the sample. The beam current absorption varies due to "electrical" heterogenities of the sample)

None of these SEM modes yielded satisfactory results for detection of surface lipid which contained the organic soluble heavy metals or had been reacted with osmic acid vapors.

The electron microprobe impacts electrons onto a sample and then detects the x-rays produced by the atoms of the sample surface. The electron microprobe is capable of detecting surface compounds of atomic weight greater than 9. Experimental studies in Phase IV have shown that the electron microprobe can be successfully used to detect surface fat in freeze dried samples which have been exposed to osmic acid vapors. The osmium present in the reacted surface lipid is detected by measuring the intensity of the x-ray lines which are characteristic for osmium. In the course of this study it was determined that to obtain optimal signals from samples containing osmium in the surface fat, it is required that:

a) the target (sample surface) be flat
b) the sample be made conductive by means of a metal coating
c) osmium stained areas be larger than the probe diameter (i.e., larger than 1-3 microns)
d) the probe scanning speed is sufficiently slow so as to yield detectable osmium x-ray signals
e) sample is aligned relative to the detector to give maximum signal intensity and an increased signal to noise ratio

With the above conditons fulfilled, the best results were obtained with aluminum as the coating metal and the detector set to read the M_{α} x-ray line for osmium (OsM_{α} line). It was observed that

aluminum was superior to gold as a coating material since gold produces x-rays of nearly the same wavelength as the OsM_{α} line, thus giving a strong background signal. It was also determined that the M_{α} line of osmium had a much lower background than the osmium L_{α} line, and thus was preferred.

2.2.2 Evaluations of Microscopic Techniques

Observations of freeze dried emulsions exposed to OsO_4 vapors showed that a good correlation existed between electron microprobe images and observations of dark stained areas in the optical microscope. Maltodextrin samples, whose surface had been partially coated with lipid, gave superimposable images for each technique. Surface areas of heavy visual staining showed strong EMP signals, while surface areas of no staining showed no signals. Freeze dried emulsions gave similar results. Emulsions which had their surface fat removed by washing with organic solvent prior to staining with osmic acid showed no darkening in the OM and no image in the EMP, even though the OM and SEM showed the presence of encapsulated lipid.

Dried maltodextrin based O/W emulsions have been found to produce good EMP images, since the sample surfaces are generally flat and there is low background since there is no reactivity between osmic acid vapors and pure maltodextrin. Microcrystalline cellulose (Avicel) does not react with osmic acid. The fat on the Avicel does react, but the curved surfaces of the microcrystals cause the osmium x-ray signals from the fat deposits to

be scattered and not caught by the detector, thereby preventing image formation. Some proteins were observed to react with osmic acid, (e.g. egg albumin) and can therefore produce EMP images. This causes an additional source of background noise for albumin based emulsions. It was noted, on the other hand, that gelatin did not react with osmic acid.

2.2.3 Structure Determination through Sequential Microscopic Observations

It has been demonstrated in Phase IV of this contract that by use of osmic acid treatments and sequential observations with the various microscopic techniques (OM, SEM and EMP), the presence of surface and encapsulated lipid in freeze dried systems can be visualized and its distribution determined. This is accomplished by the following experimental plan. The dry sample, which has been reacted with osmic acid, is first scanned in the optical microscope. It is then metal coated and observed in the SEM, followed by the EMP. The metal coated sample may then be returned to the OM for more detailed study of areas of interest as found in the SEM and/or EMP. The metal coating is sufficiently thin (10-30 nm) so that internal sample structure can be noted when viewing in the dry state or in an immersion medium. With this technique it has been possible to produce a series of micrographs of the same sample area using the above 3 microscopic methods. This ability to combine information from a variety of techniques is very important when attempting interpretation of the oil-solid

physical interrelationship since each technique alone gives only limited information. This is demonstrated by the following example taken from a Phase IV experiment.

Figures 1 and 2 show SEM and EMP images of the same grain of a freeze dried triolein (5%) and maltodextrin (20%) emulsion. Grains "flaked" from the freeze dried sample were attached to glass coverslips with double stick tape and then exposed to osmic acid vapors. Grains having a flat surface and dark staining characteristic for surface fat were selected for further study during observations in the OM. These grains are coated with aluminum and then observed in the SEM. Figure 1 shows the SEM view of a typical maltodextrin grain of relatively smooth surface, having only a few depressions and bumps. The upper left side has a rough surface appearance with a ridge running nearly parallel to and close to the upper edge. The right side shows the major grain surface with a smaller covering parallel platelet which creates a space between them. A sizable wedge-shaped crack runs diagonally through half the grain, starting at the lower left corner. The EMP photographic system produces images which are the mirror image of SEM photographs. The EMP image of the same grain as seen in Figure 1 (Figure 2) shows the fat deposits to be located along structural features of the surface. A large amount of oil was trapped between the ice and the maltodextrin phases, during freezing. Following freeze drying this oil is present as deposits along the ridge of maltodextrin in the upper part of the sample

which formed by the growing ice. Surface lipid is also present on the upper part of the smaller parallel oriented plate (right side of Figure 1); surface lipid that is trapped in the space between the two plates will not be detected in the EMP. Scattered areas of concentrated osmium signal corresponds well with surface depressions and broken bumps; the wedge-shaped crack is clearly visible in the EMP showing only background noise. At some locations the contour of the grain is sharply defined due to oil exuded from broken edges. The signal intensity across the grain surface is higher than the background, indicating that there is a thin coating of surface lipid. The upper right part of the EMP (upper left in SEM) shows only a limited osmium signal due to a) little surface fat and/or b) rough surface morphology which prevents the generated x-rays from being sent into the detector. All the observations noted above from the SEM and EMP agreed well with OM observations (not shown here).

2.3 Quantitative Evaluation of Surface and Encapsulated Lipid

2.3.1 Quantitative Analysis Technique

Methods for quantitative evaluations of surface and encapsulated lipid have been developed using sequential extractions, first a Soxhlet extraction using hexane to remove surface fat, and second, a sequential water-chloroform-ethanol extraction to determine the encapsulated fat. Quantitative evaluation of recovery of surface lipid was determined by conducting the Soxhlet extractions on coated samples of up to 2.0g oil/g malto-dextrin. Recoveries were almost always greater than 98%. A few samples,

which gave recoveries below 98%, (90-96%), were observed to have a small amount of "glassy" malto-dextrin in the bottom of the Soxhlet cup. This resulted from the solvent causing a structural transformation of the malto-dextrin. OsO_4 staining showed the presence of lipid in this "glassy" body, while the remaining porous sample showed no staining. This behavior is eliminated by control of the extraction temperature, and recoveries of surface lipid have been between 95-100%.

The sample with surface lipid removed is dispersed in water in a separatory funnel to disrupt the carbohydrate matrix and release the encapsulated oil. Chloroform is added and the funnel is shaken. Ethanol is added to improve the sharpness of the interface between the water and chloroform phases. The amount of ethanol which must be added will depend on the oil concentration, solids concentration and water and chloroform concentrations. Phase separation can be accelerated by holding the separatory funnel at 4°C for a few hours. The aqueous phase is extracted two more times and the chloroform phases pooled. The oil in the organic solution is determined by removing the chloroform from the solution by vacuum evaporation and drying overnight in a vacuum oven at 45°C. This procedure eliminates the need for filtration, which has been shown earlier to cause complications, due to absorption of oil globules on the filter and passage of some of the fine malto-dextrin particles through the filter.

2.3.2 Evaluation of Quantitative Analysis Technique

Tables 2 and 3 give typical results for recovery of lipids and quantitation of lipid location for surface, encapsulated and total lipid for malto-dextrin and Avicel based emulsions. It can be seen in Table 2 that the average recoveries for the various extraction procedures are good. With the methanol treated solutions, there is some variability between duplicate samples. In Table 3, this is reduced by first conducting the Soxhlet extraction to remove surface lipid and by use of ethanol instead of methanol. It can also be seen in Table 2 that all the triolein can be extracted from the Avicel system using the Soxhlet hexane extraction, indicating that with Avicel all the oil is on the surface.

The samples listed in Table 3 were first extracted with hexane in the Soxhlet apparatus to measure the surface oil, and then the residual powder re-extracted with water-chloroform-ethanol to measure encapsulated oil. Sample 12 was held for microscopic examination. Samples 1-8 were not measured for surface oil and thus are not reported here. With the exception of the very high recovery of sample 15, the average total recovery is good. It appears that there are two distinct percentage surface oils for these presumably duplicate samples. The close agreement within each set of values indicates that this is not due to the extraction procedures, but rather is somehow related to sample preparation.

2.2.3 Combined Quantitative and Microscopic Evaluation of Freeze Dried Emulsion

Freeze dried emulsions were examined by microscopic techniques for physical appearance and fat extraction analyses conducted for measuring surface and encapsulated lipid. An O/W emulsion (20% maltodextrin, 5.5% linoleic acid, emulsifiers) was slowly frozen at -20°C and freeze dried. The lipid distribution was analyzed for surface oil by hexane extraction in a Soxhlet and for encapsulated oil or total oil by extraction with water, chloroform, and ethanol. The results showed the following distribution:

encapsulated oil	74%
surface oil	26%
Recovery of total oil	100%

The high degree of encapsulation was confirmed by optical microscopy. Very dense concentrations of deformed oil globules were observed in practically all maltodextrin grains (Fig. 3). Exposure of dried grains to osmic acid gave only scattered darkening, indicating that the surface oil was not present as a continuous film. The areas of osmic acid staining were generally found to have a rough surface topology, indicative of ridges, depressions, grooves and closely spaced parallel flakes. Flat grains showed no surface oil, only heavy encapsulation. The roughness of these surface areas was confirmed by the SEM. The EMP showed fat concentrations only along these topological features. Examination of selected grains showed that this emulsion

kept its overall matrix structure intact upon washing with hexane to remove surface oil. Reaction with osmic acid and further microscopic studies showed that the surface oil had been completely removed from the ridges, depressions, grooves etc., while the encapsulated oil was left undisturbed.

The fresh emulsion had oil droplet diameters of generally 1-3 microns. The behavior of the emulsion during handling and the high degree of encapsulation during freezing indicated that the emulsion was quite stable. Rehydration of the freeze-dried emulsion which had its surface oil removed by the hexane extraction gave a solution with most droplets in the 1-3 micron range, though a number of droplets as large as 10 microns were observed. When freeze-dried emulsion with surface oil present was rehydrated, the majority of droplets were still about 1-3 microns in diameter, though in this case a number of large droplets having diameters up to 35 microns were present. It is assumed that this is due to agglomeration and coalescence of droplets when present as surface oil.

The above results indicate that the surface oil consists of droplets that were too large to be fully encapsulated by a protective maltodextrin wall during the freezing process.

2.4 Effect of Process Variables on Structure of Freeze Dried Emulsions

2.4.1 Effect of Sample Composition

Triolein emulsions (5% oil) were prepared using a variety of structure forming solutes at 20% solids. The solutes included

glycine, gelatin, egg albumin, starch, carboxy-methyl cellulose (CMC). The freeze dried materials were observed in the OM before and after osmic acid staining, and in the SEM and EMP. Table 1 summarizes some of the principal observations. Surface "stickiness" is due to lipid on the surface which causes the flakes to adhere to one another. The darkness of the osmic acid staining was correlated with the EMP image strength (except in the case of starch where the spherical granules do not give good directional reflection of the x-rays to the detector). The egg albumin emulsion gives dark staining with osmic acid and an EMP image, although the product is termed "non sticky". The EMP for the egg albumin samples shows no locally stained areas, but rather a uniform weak signal intensity over the whole surface. This shows that the staining reaction which took place was due not only to possible surface fat but also to an egg albumin-osmic acid reaction. A test showed that pure egg albumin will react with osmic acid to form a colored stain.

2.4.2 Effect of Freezing Rate on Freeze Dried Emulsion Structure

In initial experiments maltodextrin emulsions (20% solids) containing triolein at 1% or 5% were frozen in a cold room at -20°C (slow freezing) or in liquid nitrogen (fast freezing). Slowly frozen samples showed less osmic acid staining than the respective rapidly frozen samples, and a higher degree of encapsulated lipid for the 1% emulsion. At 5% triolein the inclusion

densities appeared very similar for both freezing rates. Freeze dried emulsions containing linoleic acid instead of triolein showed similar behavior (i.e., the slow frozen showed less osmic acid staining than rapidly frozen (liquid nitrogen) samples and the packing density of the encapsulated oil was higher). These results indicate that more lipid is encapsulated into the matrix forming solute with slow freezing than with fast freezing.

2.4.3. Freezing Rate Studies with Microscopic and Quantitative Evaluations

Emulsions at lower oil phase volumes were evaluated for the influence of freezing rate on structure. A system consisting of 20% maltodextrin, 1.0% linoleic acid and emulsifiers was homogenized and freeze dried after being frozen slowly at -20°C or frozen rapidly with liquid nitrogen. Extensive optical microscopic studies were conducted on the dried O/W emulsions. Oil distribution was quantitatively evaluated by the methods described in Section 2.3.1:

A) Determination of total oil by extraction of dried O/W emulsion with a water/chloroform/ethanol system;

B) Determination of surface oil by Soxhlet extraction using hexane, followed by determination of encapsulated oil by extraction with water/chloroform/ethanol.

The freshly prepared emulsions had oil droplet diameters about 1-2 microns and below. The following results were obtained

for the freeze dried emulsions.

2.4.3.1 Emulsion frozen at -20°C

encapsulated oil	21%
surface oil	79%
recovery of total oil	100%

The dried emulsion was noted to be very porous. In the optical microscope nearly all maltodextrin grains were smooth, thicknesses averaging 8-12 microns. The grains contained spherical oil inclusions of diameters ≤ 10 microns (Fig. 4). The relatively high content of surface oil was easily demonstrated by exposing dried grains to osmic acid vapors. It was observed that besides concentrated staining along surface characteristics (i.e. surface depressions due to ice dendrites, grooves, ridges, etc.) a light but distinct uniform staining covered nearly all grains, indicating the presence of a continuous film of oil (Fig. 5).

While rehydration of this freeze dried emulsion gave a dispersion with most oil globules having diameters around 1-2 microns, a noticeable number of droplets having larger diameters, up to 35 microns, were observed. When freeze dried emulsion which had its surface oil removed by soxhlet extraction was rehydrated, the average globule size was still around 1-2 microns, but no droplets larger than 12 microns were found.

2.4.3.2 Emulsion frozen with liquid nitrogen

encapsulated oil	35%
surface oil	65%
recovery of total oil	98%

The freeze dried rapidly frozen emulsion had a very dense and nonporous cake. In the optical microscope the grains were very thin (2-5 microns) with a very rough surface topology due to narrowly spaced ridges (1-5 microns apart) (Fig. 6). The oil inclusions were spherical with diameters 5 microns. Upon exposure to osmic acid, surface oil was visible only as isolated dark stained areas, usually where one set of ridges led into another set of ridges oriented at another angle (Fig. 7). It was also observed that a very weak staining seemed to cover the grains as partially continuous layers, indicative of deposits of very thin films of oil.

Rehydration of the freeze dried emulsion showed average oil globule sizes around 1-2 microns, with a few with diameters up to 13 microns. Rehydration of emulsion previously freed of surface oil by soxhlet extraction gave oil globules of diameters not more than 5 microns.

The above results indicate that the emulsion was not quite stable during freezing. At the slow freezing rate (10 ml samples freezing completely in an hour at -20°C) oil droplets presumably had time to agglomerate and coalesce to give droplet sizes large

enough to exclude them from incorporation in the concentrated solute phase (CSP), thus forming surface deposits. The formation of larger clusters and globules of oil means that an even larger fraction of the oil cannot be encapsulated in the CSP, although the final thickness of the slow frozen CSP should allow larger oil globules to be entrapped than would be possible with the thinner CSP for a fast frozen emulsion.

The results also indicate that the emulsion was not quite stable when freezing with liquid nitrogen (10 ml samples freeze in about 15 seconds). The amount of oil encapsulated was higher (35% versus 21%) since during the fast freezing period the oil globules did not have enough time to destabilize into globules large enough to be excluded from the CSP. This explains the somewhat unexpected result that fast freezing yielded better encapsulation of oil than slow freezing in these experiments.

Table 1

Microscopic Evaluation of Freeze Dried Triolein Emulsions

	Matrix structure	Incorporated droplets	Droplets upon rehydration	Sticky surface	OsO_4 Stain	EMP image
glycine	anisotropic plates needles	no	yes, many	very	very black	---
egg albumin	flaky platelets	numerous tiny	yes	no	dark	low
gelatin	hard honeycombed network	many tiny	matrix swells slow release	no	white	none
soluble starch*	intact granules	none	many appear	very	very dark	none
CMC	rubbery plates	many small	some	no	light	weak

*On examination shows that "soluble starch" was not pregelatinized (as expected) and was not heated sufficiently to gelatinize during preparation.

Table 2

Recovery of Lipids from Freeze Dried Emulsified Systems

Emulsified System [a]	Experiment Number	% of Theoretical Oil Recovered [b]	Average % Recovered
1/2 % triolein [c]	1	116.5	
20% maltodextrin	2	111.0	106.2
	3	91.2	
1% triolein [c]	1	87.4	100.6
20% maltodextrin	2	113.8	
2% triolein	1	96.6 [e]	99.7
20% maltodextrin	2	102.7 [f]	
2% triolein [d]	1	101.5	
10% Avicel	2	100.9	101.7
	3	106.2	

[a] Concentrations given are for initial emulsion

[b] Theoretical based on dry sample weight and initial emulsion composition

[c] Methanol used to sharpen interphase interface during extraction

[d] Extraction with Soxhlet apparatus using hexane (i.e. surface fat)

[e] Ethanol used to sharpen interpahse interface during extraction

[f] Two step extraction: Soxhlet with Hexane (surface) 94.4% of theoretical

H_2O-chloroform-ethanol 8.3% of theoretical
(encapsulated)

Table 3

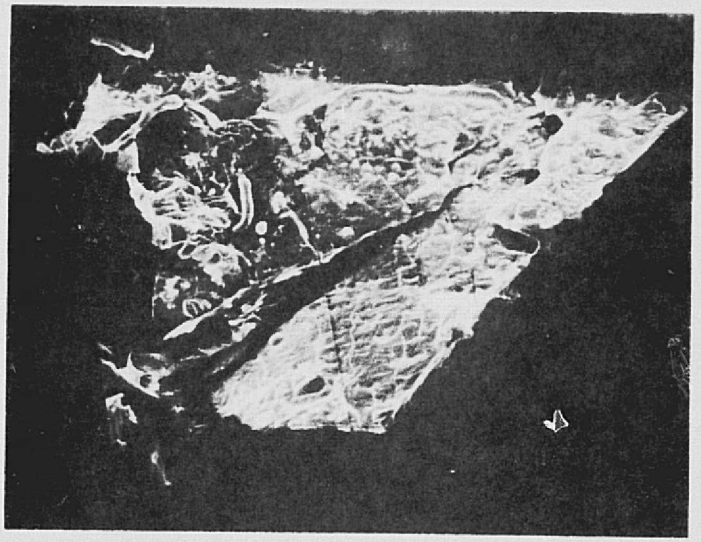
Lipid Location in Slowly Frozen freeze dried

1% Linoleic Acid, 20% Maltodextrin Emulsions

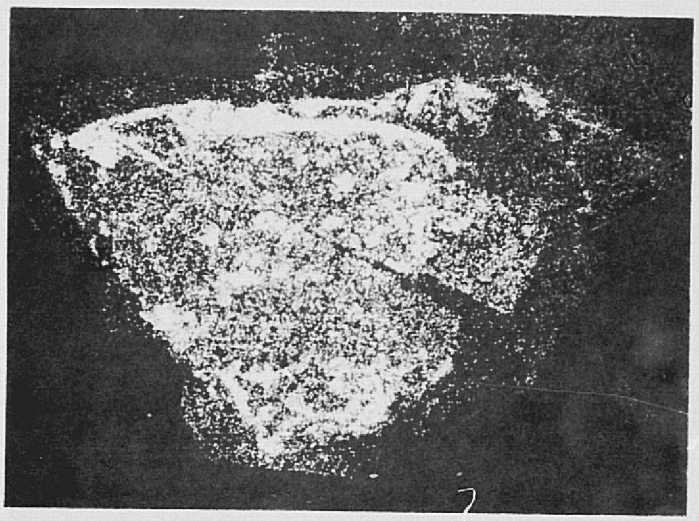
Sample Number	% of Theoretical oil recovered [a]	surface oil (% of total recovered)	encapsulated oil (% of total recovered)
9	105.8	54.4	45.6
10	96.9	50.7	49.3
11	97.1	74.0	26.0
13	94.8	76.0	24.0
14	91.7	54.4	45.6
15	140.5	72.6	27.4

[a] Theoretical based on dry sample weights and initial oil composition

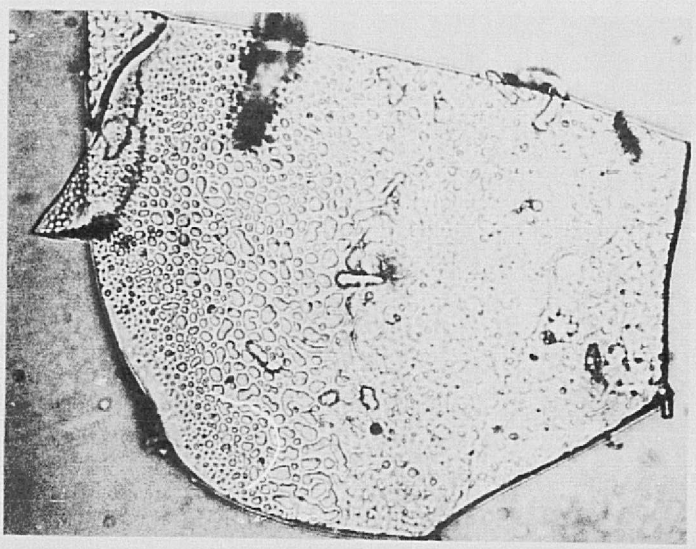
List of Figures



①

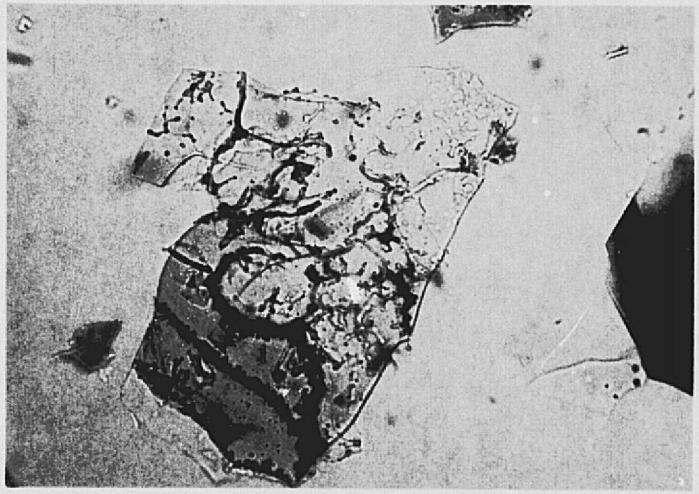


②



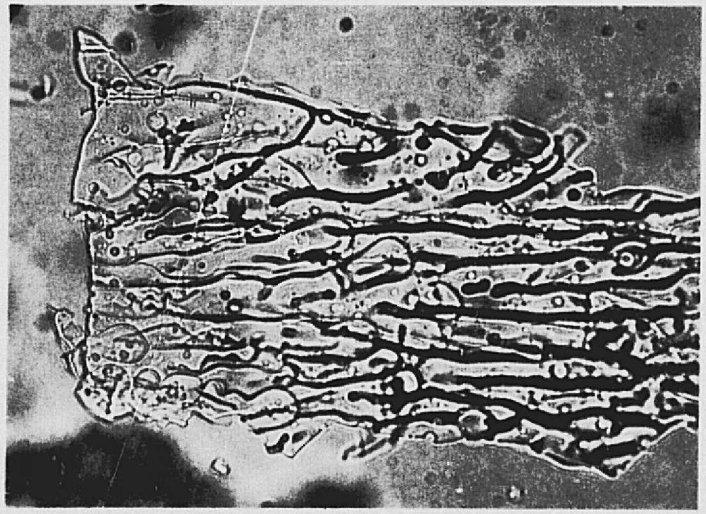
③

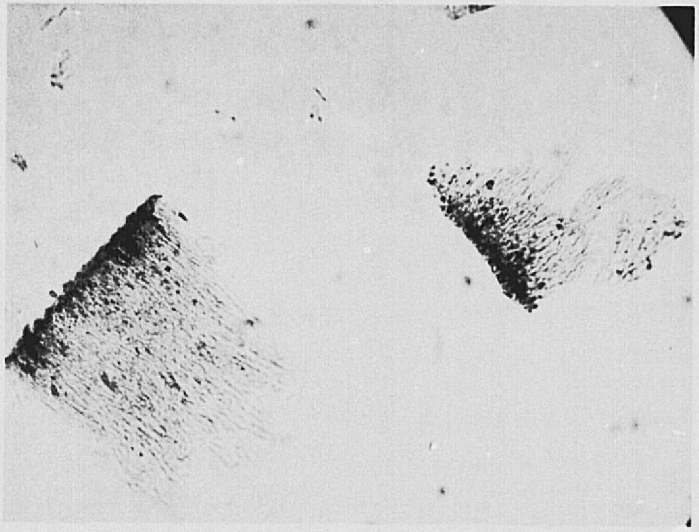
④



⑤

⑥





⑦

3. Investigations of Structural Changes in Freeze Dried Systems

Transformations of structure of dehydrated materials are quite important, as many factors affecting product quality are related to such changes. This is especially true with freeze dried foods where retention of structure through the drying process is considered a significant advantage of this process. The phenomenon of "collapse" is a structural transformation of the freeze drying material which results from the viscous flow of the frozen and/or partially dried matrix. Other phenomena which strongly influence product acceptability, such as caking, loss of flavor, visual acceptability and perhaps nutrient stability are also related to this behavior. Knowledge about viscous flow in drying and dehydrated products and factors affecting its occurrence is needed for development of processes and products of improved quality.

Our studies in this area during the Phase IV period are described in the following technical articles "Loss of Structure in Freeze Dried Carbohydrate Solutions: Effect of Temperature, Moisture Content and Composition" which has been accepted for publication by the Journal of the Science of Food and Agriculture.

Loss of Structure in Freeze Dried Carbohydrate Solutions: Effect of Temperature, Moisture Content and Composition

by

Spyros Tsourouflis, James M. Flink and Marcus Karel

Department of Nutrition and Food Science

Massachusetts Institute of Technology

Cambridge, Massachusetts 02139

Send proofs to:
Prof. James M. Flink
M.I.T. Room 56-109
Cambridge, MA 02139
U.S.A.

Contribution No. 2695 of the Department of Nutrition and Food Science

Abstract

During processing and storage, dehydrated food materials are subject to changes in their structure. Terms used to describe these changes, which are due to the same basic phenomena, vary from process to process. Thus, during freeze drying, loss of structure is called "collapse", while during storage, phenomena related to viscous flow of the dried powder matrix are termed "stickiness".

This loss of initial structure often results in the loss of desirable product qualities, though in some cases controlled manipulation of these changes is used to produce improved products. In freeze drying, collapse of capillaries in the dry layer results in puffing and loss of desirable structure. In dehydrated powders "stickiness" leading to caking and other defects is also a result of collapse phenomena.

The collapse temperature of freeze dried orange juice and carbohydrate solutions was investigated as a function of moisture content and sample composition. It was observed that collapse temperature decreased as the sample moisture content increased. Mixtures of materials collapsed at a temperature intermediate to that of the individual components. The consequences of these observations to a number of food processes are discussed.

Introduction

Changes in structure (macroscopic or microscopic) of dehydrated materials in response to environmental stresses has been reported in the literature for a number of situations. While it appears that these structural changes are manifestations of the same basic phenomena (time, temperature and moisture dependent viscous flow), a variety of expressions which describe sensory behavior of the materials are used in the literature. (Throughout this paper we will use the term "collapse", which has been used to characterize loss of structure during freeze drying.)

It is noted in the literature that some products undergo "COLLAPSE" during freeze drying when the frozen sample temperature is higher than some characteristic temperature, called the collapse temperature (T_c). For various aqueous solutions, collapse temperatures vary over a wide range, from -5 to -60°C.[1,2,3] A collapsed product loses its shape by becoming a highly viscous liquid and often shows poor aroma retention, poor rehydration characteristics and uneven dryness. When collapse occurs during freeze drying, ice crystals appear to dissolve rather than to sublime, resulting in obliteration of capillaries and thus an increased vapor flow resistance. Extreme collapse completely closes the capillaries, so that moisture removal is limited to evaporative mechanisms, with much bubbling and spattering.[1,2]

A number of cases of structure transformation from dried products to the viscous state due to added moisture and/or increased temperature are of importance in industrial practice. Concentrated liquid foods such as tomato juice and concentrated orange juice often show problems during spray drying due to "STICKINESS" of the drying particles. Scorching of particles sticking to the walls of dryers, and difficulties in collecting powder in the collecting zones are a consequence of this stickiness. The "STICKY-POINT" temperature marks a transition from a stable dry powder to a viscous state and is thus related to collapse.[4,5]

Instantizing of powders by "AGGLOMERATION" is also related to collapse. This process depends on controlled raising of the moisture content of surfaces of powder to a level which makes these surfaces sticky at the desired temperature. The wetting is conducted under conditions which result in the particles sticking together in clusters, which are then dried to the desired moisture content.[6]

"CAKING" of foods during storage is also related to collapse. Pisecky[7] observes that when sufficient moisture is present, sintering of dried particles can occur, which results in the loss of the powder character for the material. Again, the moisture and temperature dependent transformation to the viscous liquid is responsible for this physical change.

During storage, optimum moisture and temperature conditions must be maintained to avoid structural change of the material and the resultant loss of desirable product

properties. For the design of spray drying or agglomeration processes, it is necessary to understand the dependence of "sticky-point" temperatures on moisture contents.

Recently, theories have been developed to explain collapse phenomena occurring during freeze drying. One of these theories, the Amorphous Viscosity Theory[8], appears to be utilizable to describe collapse pheomena in general, if it is remembered that particular critical values of environmental parameters will be very different for the different situations considered.

The explanation of collapse phenomena occurring during freeze drying is based on phase transition phenomena which occurs during the initial step of freezing. During freezing, most compounds of interest in foods, such as sugars for example, do not nucleate and formation of solid eutectic mixtures does not occur; rather the solution becomes more concentrated as water is transferred to ice crystals. According to MacKenzie[2] and White and Cakebread[9], at sufficiently high solute concentration, which during freezing coincides with attainment of low temperatures, the remaining solution will undergo a glass transition and no more ice is formed. The Amorphous Viscosity Theory of Collapse considers the matrix as a concentrated amorphous aqueous solution. As long as the temperature of the solute matrix is below some critical value, the collapse temperature, the matrix is sufficiently viscous to behave like a solid. This viscosity

is related to the combination of solids content (i.e., moisture content) and temperature, which for the case of the frozen material, are both related to temperature. If the temperature of the frozen zone rises above the collapse temperature, the concentrated amorphous solution becomes less viscous because of dilution with water due to ice melting, as well as because of the direct effect of temperature on viscosity.[1] As water is removed during the drying, the matrix becomes more rigid and can tolerate higher temperatures without undergoing viscous flow.

As noted in the description of STICKINESS, etc. above, the phenomena associated with changes in the structure of "dry" materials are also related to combined temperature and moisture stresses, just as is indicated in the Amorphous Viscosity Theory of Collapse.

We have studied collapse phenomena of freeze dried carbohydrates and of orange juice as a function of moisture and temperature. The use of additives to raise the collapse temperature or to increase the moisture content at which collapse occurs at a given temperature was also studied.

Experimental

Systems studied included orange juice, with or without addition of various carbohydrates, and solutions of several carbohydrates. Commercial frozen concentrated orange juice was used and was reconstituted according to manufacturer's instructions. The sources of the carbohydrates used are shown in Table 1.

Solutions of the carbohydrates in water or in the orange juice were prepared in the desired concentrations, and 2 ml aliquots were delivered with a syringe to pre-weighed 5 ml ampules. The samples were then frozen with the ampules in a tilted position so that a greater surface area could be obtained. This improved the rate of the subsequent freeze drying and humidification steps and also aided the visual determination of collapse. The samples were either slowly frozen (overnight at 0°F) or rapidly frozen in liquid nitrogen. Following freezing, the samples were freeze dried for 48 hours. The weight of freeze dried solids was determined for each sample.

The samples were then humidified to different moisture contents ranging from about 0% to 10%. In a typical experiment, 7 to 8 samples of different moisture content were used. The humidification was conducted at 32°F to avoid collapse during sample conditioning. Samples were humidified by either holding for different lengths of time in an evacuated desiccator containing a saturated solution of K_2SO_4, maintaining a constant relative humidity of 97%, or by holding the samples for a fixed time period over a series of constant humidity solutions ranging from 11% RH (LiCl) to 97% RH (K_2SO_4).

After humidification, the ampules were carried in ice to the analytical balance, where the water pick up was determined gravimetrically. Moisture uptake is expressed as

as percent of total weight of dry solids in the ampule. Freeze dried samples were defined as free of water and all subsequent uptakes are relative to this zero basis. Immediately after weighing, the neck of the ampule was flame-sealed while the body of the ampule was kept cool by holding it in a chilled wet cloth.

For determination of collapse temperature, two identical water-baths were used to evaluate the temperature of the samples in 10°F increments. While the samples were being held at a constant temperature in one of the water baths, the other was equilibrating to the next desired temperature, 10°F higher. The elevation of temperature was continued until all samples had collapsed or until the maximum temperature of the bath was reached (210°F). An oil bath or an oven was used for temperatures above 210°F. Collapse was observed visually and was defined as the change of the appearance of the sample's surface. The collapsed sample resembles a highly viscous, glassy material compared to the pre-collapse appearance which is that of a porous solid. It is to be expected that for a dynamic phenomenon involving flow of viscoelastic materials, the evaluation of collapse will depend on the length of time allowed for observation[10]. At a given moisture, the rate of the transformation step will vary with temperature so that, for a given extent of transformation (i.e., the not collapsed/collapsed boundary) the collapse temperature determined will

depend on the time period used. A preliminary test showed that for our system, the time required for collapse varied with holding temperature as shown in Figure 1. The converse of this observation means that for holding times over 45 minutes, the collapse temperature remains relatively constant at its lowest value for a given moisture content. For this reason, samples were held 45 minutes at each temperature for the determination of collapse. If collapse occurred prior to the end of this holding period the collapse temperature was estimated by an interpolation, which assumed that a linear relation between collapse temperature and time, within the narrow specified limits (time interval = 45 minutes; temperature interval = 10°F) was a sufficiently accurate model of the expected more complex exponential behavior.

Thus the estimated collapse temperature (T_c) was obtained by using equation (1):

$$T_c = T_B - \left(\frac{t_c}{45}\right)(10°F) \qquad (1)$$

where T_B = Bath temperature (°F)

t_c = Time in minutes to collapse following the transfer to bath maintained at T_B from bath maintained at T_B-10°F.

Results

Collapse temperatures for several of the systems studied are presented in Table 2. These temperatures were obtained on materials in dry state. Collapse temperature dependence on moisture content was also studied in a number of systems. Figure 2 shows the moisture content dependence of the collapse temperature for maltose. The collapse temperature of dry maltose is high: 205°F. The mode of freezing has only a slight affect on the collapse temperature of the rehumidified freeze dried material. For maltose, the slowly frozen samples show a slightly higher collapse temperature at all moistures than the fast frozen samples. In experiments with lactose, we observed a reverse behavior with slowly frozen samples having a slightly lower T_c.

The dependence of T_c on moisture content in a mixture of sucrose and maltose is shown in Figure 3. The data are typical of those obtained with binary mixtures of sugars. The collapse temperature of the mixtures are typically intermediate between the temperatures for the two individual components.

The maltodextrins used in this experiment, (Maltrins: M-100, M-150, M-200, M-250) all have a high collapse temperature (Figure 4). The collapse temperature is a function of the dextrose equivalent (D.E.) of the maltodextrin. Maltrins with higher D.E., that is, with a lower average molecular weight, show a lower collapse temperature (M-250 at 400°F) while Maltrins with lower D.E. (higher average

molecular weight) have a higher collapse temperature (M-100 at 480°F). Maltrins with intermediate D.E. collapse at intermediate temperatures. The rate of freezing was not found to have any effect on the collapse temperature of Maltrins.

As shown in Figure 5, the collapse temperature of pure orange juice is relatively low, the dry juice collapsing at 125°F. This collapse temperature is very close to that of sucrose (132°F) which is not unexpected since orange juice has a high content of sucrose. According to Bellows[8], 50% of the sugar present in orange juice is sucrose.

In this case, freezing rate has relatively little influence on collapse temperature. The low collapse temperature observed for the freeze dried orange juice is directly associated with the difficulties encountered in preparing the dried material. During the initial steps of freeze drying, there is some melting and puffing; however, there is sufficient unpuffed material to allow determination of the collapse temperature.

Four Maltrins (M-100, M-150, M-200 and M-250) were added to orange juice at different concentrations and the change of collapse temperature with maltrin concentration was studied. Collapse was studied only at 0% moisture. As Figure 6 shows, there is a considerable effect of added maltodextrins on the collapse temperature of dry juice. It can also be seen that the collapse temperature changes with

average molecular weight of the Maltrins. Low D.E. Maltrins give higher collapse temperatures for the orange juice mixture than high D.E. Maltrins at the same concentration.

Figure 7 shows the increase in collapse temperature of orange juice with increasing concentration of gum arabic, again only for 0% moisture samples. There is a considerable increase in collapse temperature and it is affected by the mode of freezing.

Karaya gum has the same affect on collapse temperature at all concentrations tested (up to 4%). As Figure 8 shows, a small amount of Karaya gum (around 0.5%) elevates the collapse temperature of orange juice from 125°F to 152°F, and the T_c then remains constant for the whole range of concentrations from 0.5% to 4%. The mode of freezing does not affect the collapse temperature. Tragacanth gum behaves much the same as Karaya gum, but the elevation of collapse temperature is much higher (Figure 8).

Discussion

The results presented here have described conditions under which dehydrated food materials will undergo loss of structure. The loss of structure is presumably related to the reduction of product viscosity such that under the influences of a variety of forces (gravity, surface tension etc.) the matrix materials are able to undergo viscous flow. For a particular sample, it appears that a critical level of viscosity exists, and that this viscosity can be achieved by various combinations of moisture content and temperature. Furthermore, within limits, the evaluation of the critical limit of viscosity will depend on the time permitted for observation. Thus, if a shorter time is permitted, it was noted in Figure 1 that a higher sample temperature (i.e. lower viscosity) was required to obtain "collapse."

It was noted that the higher the concentration of the initial solution, the higher the collapse temperature. The initial solute concentration determines the amount of water which remains unfrozen at any given temperature, with concentrated solutions forming less ice than more dilute solutions. The space occupied by ice in the frozen material will ultimately become part of the system of pores and other voids in the dried matrix, provided that no collapse during freeze drying occurs. Presumably, a system with a smaller fraction of total volume occupied by voids is more resistant to collapse. Less voidage means a smaller number of

capillaries, and, therefore, less internal surface area. If surface tension is the driving force for collapse, this would lead to higher collapse temperatures. However, there is an upper limit to the use of preconcentration as a means of achieving higher collapse temperatures, because higher concentrations inhibit ice nucleation.

The rate of freezing for sample preparation appears to have a significant, but relatively small, influence on collapse temperature for solutes of low molecular weight, though the pattern of behavior for the samples studied is not always the same, even for similar materials such as disaccharides. Freezing rate differences can be considered in terms of nucleation and growth rates of ice crystals. Nucleation rate influences the number of ice crystals formed, and, therefore, the relative sizes of ice crystals (subsequently the pores) and the matrix thickness. Fast freezing increases the number of nuclei formed and means that the distance between ice crystals decreases and therefore the thickness of the matrix decreases. There is the distinct possibility that similar molecular species such as disaccharides will form different bonding arrays on the molecular level. Indeed, in studies in our labs, we see that the crystal form for sucrose is quite different from that for lactose or maltose[11]. In this case, the effect of thinner matrix lamella on overall matrix strength can be quite variable from material to material, giving a

complex behavior for the effect of freezing rate on collapse temperature, as observed.

Molecular weight (M.W.) plays a role in affecting T_c, but is not the sole determinant. In Maltrins, T_c increases with M.W., and the T_c's of the Maltrins are also higher than those of disaccharides. However, different disaccharides with the same M.W. show different T_c values, which, as noted above, may be due to differences in strengths of bonding arrays of the different disaccharides.

Addition of high molecular weight polysaccharides to orange juice resulted in substantial increases in collapse temperature, presumably through increasing the system viscosity. This observation is of practical significance, since for some of the gums tested, significant increases in product structural stability can be obtained with the addition of only small amounts of the gum. This will lead to increased storage life with respect to quality deterioration associated with structural changes (solubility, caking, etc.) and/or to decreased package costs to obtain a given shelf life.

The Amorphous Viscosity Theory of Collapse, which has been developed on the basis of study of the freeze drying behavior of solutions, has as its critical variable, the viscosity of the matrix material. Bellows and King[1] reported the critical range of matrix viscosity (called the concentrated amorphous solute) to be between 10^7 and

10^{10} cP (the techniques for measuring the viscosities in this range are quite slow). When the collapse temperatures for freeze drying materials were included with the data presented here for freeze dried materials, a smooth curve was obtained. When this pooled data was plotted as ln moisture content vs. temperature or ln moisture content vs. reciprocal of the absolute temperature, straight lines were obtained (Figure 9). This indicates that the same critical viscosity range is applicable to both collapse phenomena. Similarly, when the data of Brennan, et.al.[4] for STICKY-POINT temperatures is treated in a similar manner, a similar relationship is obtained.

These observations seem to indicate a simple rapid way for determining the collapse temperatures for concentrated liquid food systems. The collapse temperatures are determined for a number of moisture contents and the results plotted as in Figure 9. Extrapolation of this curve and combination with the freezing point-concentration curve will give a measure of the collapse temperature for the frozen material.

It was also noted that in earlier studies on loss of model flavor compounds from freeze dried materials, a critical temperature for release of the volatile from the dry matrix was found. Chirife and Karel[12] noted that encapsulated 1-propanol was not released from freeze dried maltose at temperatures up to 82°C, but that partial release was obtained at 100°C. In this study, it has been

found that the collapse temperature for dry maltose is 96°C (205°F). Thus, release can be related to the loss of structure. A similar observation was reported by Flink and Karel[13] for humidification of volatile containing maltose at low temperature. Their temperature-moisture combination giving loss of volatile lies on the collapse curve of maltose as shown in Figure 9.

While the theory of collapse phenomena has been discussed in literature primarily in connection with freeze drying of foods, the results on collapse temperatures obtained in this work are equally applicable to other aspects of food processing.

In agglomeration of dried powders, it is necessary to attain a slight, controlled degree of collapse of the particle surfaces, so that the surface of powder becomes sticky, yet the powder particles remain as discrete units. Examples are given by Jensen[14]. In a method for the industrial production of whey powder (75% lactose) the spray dryer operates at a low temperature in order to avoid caking of the whey powder while a controlled agglomeration is achieved after the initial drying by increasing moisture content of the powder and then redrying it. Other methods of agglomeration use water vapor to produce a controlled surface collapse which causes the particles to form clusters. These procedures are based on

the knowledge that moisture content and temperature determine the potential for collapse. The exact relationship of moisture and temperature for collapse of food materials is required for the design of agglomeration processes which will yield products of high quality. The present study shows these relationships for a number of food materials.

While for agglomeration it is desired to achieve a slight, controlled degree of collapse, in other situations, prevention of collapse is the goal. The sticking of powder in the drying and collecting zones of a spray drier is related to the collapse phenomenon. Lazar, et. al.[5], working with tomato juice, passed cooled, atmospheric air of low humidity over the walls of the drier to reduce product sticking and scorching. Their approach utilized the fact that conditions of low moisture and temperature will prevent collapse. Again, the research conducted in this study provides quantitative information on how the factors of temperature and moisture interact for a number of materials. In addition, the data on the effect of incorporation of additives on "stickiness" allows design of formulated systems which can be more successfully dried.

Another area in which prevention of collapse is essential is the maintenance of quality of dried products during storage, such as prevention of caking of dry

powders during storage and loss of flavor compounds from dried materials. Both are associated with collapse behavior[7,13].

In this study it has been shown that addition of macromolecules increases the collapse temperature of freeze dried orange juice. Some of the macromolecules studied gave large increases in collapse temperature at low levels of addition. The observed increase of collapse temperature means that the product will tolerate higher temperatures at a given moisture content without loss of structural qualities. Further, a product packaged in materials of a given water permeability will require more time to reach the critical moisture level for collapse and will therefore have a longer storage life. The above principles apply to other juices and beverages with low collapse temperature, though the collapse temperature of any juice-additive mixture will vary. For example, Moy[15] has shown that added corn syrup or maltodextrins raised the T_c of various tropical fruit juices. Stern and Storrs[16] have shown that the addition of lactose or low-dextrose corn syrup raised the collapse temperature of juices.

Acknowledgement

This study was supported in part by Contract 9-12485 from the Johnson Spacecraft Center, NASA, Houston, and in part by Research Grant No FD-00050 from the Food and Drug Administration.

References

1. Bellows. R.J. and King, C.J., Cryobiology, 1972,9,559.

2. MacKenzie, A.P., Bull. Parenteral Drug Assoc.,1965,20(4),101.

3. Ito, K., Chem. Pharm, Bull., 1970,18(8),1509.

4. Brennan, J.G., Herrera, J. and Jowitt, R., J. Fd. Technol., 1971,6,295.

5. Lazar, M.E., Brown, A.H., Smith, G.S., Wong, F.F. and Lindquist, F.E., Fd. Technol., 1956,10,129.

6. Masters, K. and Stoltze, A., Food Eng., 1973,45(2),64.

7. Pisecky, J., Non-Caking Whey Powder, Brochure No. S-188, Niro Atomizer Ltd. (Copenhagen), 1973,5 pp.

8. Bellows, R.J., Freeze Drying of Liquid Foods: Dependence of Collapse Temperature on Composition and Concentration, Ph.D. Dissertation, 1972, University of California, Berkeley.

9. White, G.W. and Cakebread, S.H., The Importance of the Glassy State in Certain Sugar-Containing Food Products, In: Proceedings of the First International Congress on Food Science and Technology, Volume 1, Gordon and Breach Science (New York), 1962, p.227.

10. Vrentas, J.S., Jarzebski, C.M. and Duda, J.L., AIChe J., 1975,21(5),894.

11. Gejl-Hansen, F., Personal Communication.

12. Chirife, J. and Karel, M., J. Fd. Technol., 1974,9,13.

13. Flink, J.M. and Karel, M., J. Fd. Technol., 1972,7,199.

14. Jensen, J.D., Fd. Technol., 1975,29(6)60.

15. Moy, J.C., J. Fd. Sci., 1971,36,906.

16. Stern, R.M. and Storrs, A., Methods of Drying Sugar Containing Materials, U.S.P. 3,483,032,1969.

Table 1

Carbohydrates used in the study

Carbohydrate	Grade or type	Source
Lactose	D(+)-Lactose, Monohydrate Powder, Reagent	J.T. Baker Chemical Co., Phillipsburg, N.J
Maltose	Powder, Reagent	Fisher Scientific Co., Fairlawn, N.J.
Sucrose	Crystals, Reagent	MCB, Norwood, Ohio
Maltrin-100	Maltodextrin, Ave. D.E. = 10	Grain Processing Co., Muscatine, Iowa
Maltrin-150	" " = 15	"
Maltrin-200	" " = 20	"
Maltrin-250	" " = 25	"
Starch	Soluble Starch, Reagent	Merck and Co., Inc., Rahway, N.J.
Gum Arabic	A-12	Stein, Hall and Co., New York, N.Y.
Locust Bean Gum	175 Mesh	"
Tragacanth Gum	Powder, T-500	"
Karaya Gum	Powder, K-1	"
Tapioca Dextrin	Powder, K-Dex 4484	"

Table 2

Collapse temperatures of freeze dried systems*

System	MW	Viscosity, cp	T_c, °F
Lactose, 25% w/v	342	2.2	214
Maltose, 25% w/v	342	2.2	205
Sucrose, 25% w/v	342	2.2	132
Sucrose-Lactose, 12.5%-12.5%	342	2.0	174
Sucrose-Maltose, 12.5%-12.5%	342	2.1	164
Maltrin-100, 25% **	1710	6.2	480
Maltrin-150, 25%	1140	3.4	450
Maltrin-200, 25%	855	3.3	450
Maltrin-250, 25%	684	3.1	400
Orange juice, 14.2% w/v	277	4.0	125
Orange juice + 10% maltose	283	4.8	150
Orange juice + 2% starch	-	4.1	128
Sucrose + 2% starch	-	2.3	164
Orange juice + 3% M-100	320	5.1	167
Orange juice + 5% M-100	349	5.4	173
Orange juice + 10% M-100	420	7.1	183
Orange juice + 15% M-100	492	8.3	192
Orange juice + 20% M-100	564	11.6	212
Orange juice + 25% M-250	287	4.7	137
Orange juice + 5% M-250	297	5.4	145
Orange juice + 10% M-250	317	6.7	155
Orange juice + 15% M-250	338	7.1	164
Orange juice + 20% M-250	358	9.3	183
Orange juice + 1% Gum Arabic	-	6.5	135
Orange juice + 3% Gum Arabic	-	12	142
Orange juice + 6% Gum Arabic	-	13	180
Orange juice + 3% Locust Bean Gum	-	1060	212
Orange juice + 3% Tragacanth Gum	-	>2000	210
Orange juice + 3% Karaya Gum	-	>2000	152
Orange juice + 3% Tapioca Dextrin	-	7.4	152
Orange juice + 6% Tapioca Dextrin	-	8.0	153
Orange juice + 10% Tapioca Dextrin	-	9.9	174

* All concentration and viscosity date refer to solutions prior to freeze drying. The T_c is for systems in the dry state.

** Molecular weights of all Maltrins are based on oligosaccharide distribution data supplied by manufacturers.

Figure Legends

Figure 1 Time required for collapse when holding dry sucrose at specified temperatures. (Sucrose freeze dried from 25% solution, fast freezing was used).

Figure 2 Collapse temperature vs moisture content for maltose (25% solids, fast and slow freezing).

Figure 3 Collapse temperature vs moisture content for a mixture of sucrose-maltose (12.5%-12.5% solids).

Figure 4 Collapse temperature vs moisture content of maltodextrins (25%, w/v).

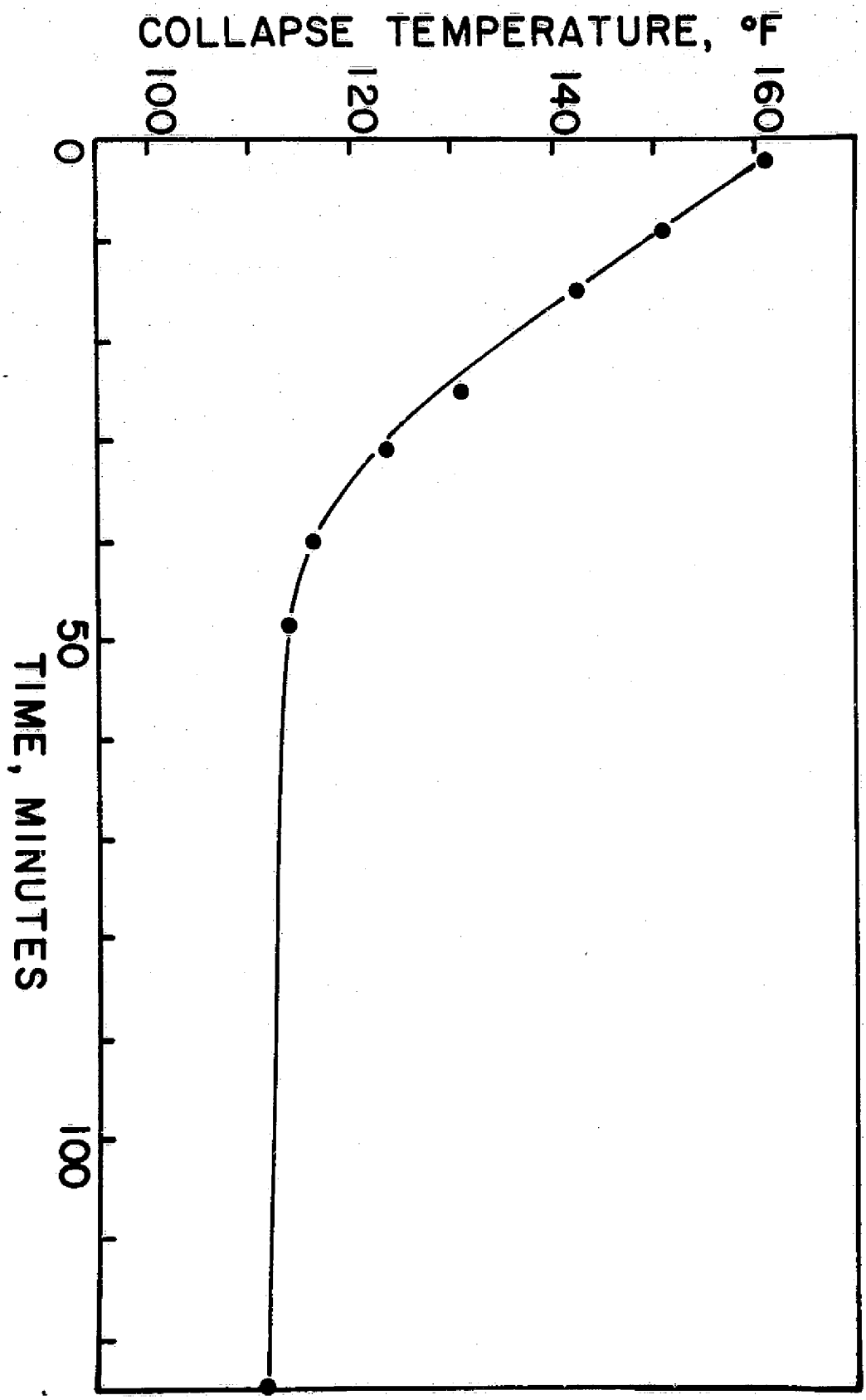
Figure 5 Collapse temperature vs moisture content for orange juice (14.2% solids).

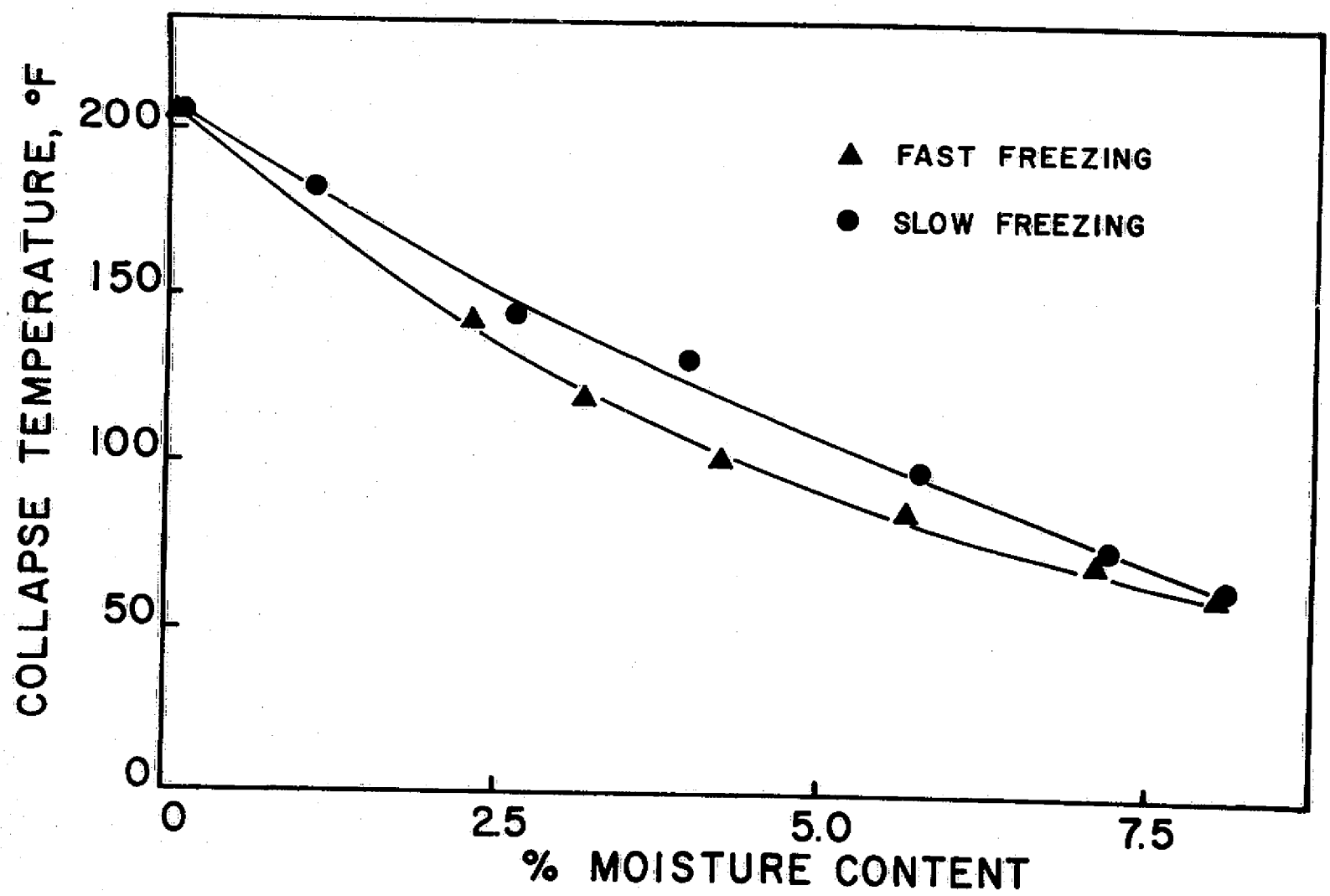
Figure 6 Collapse temperature vs concentration of maltrins in orange juice.

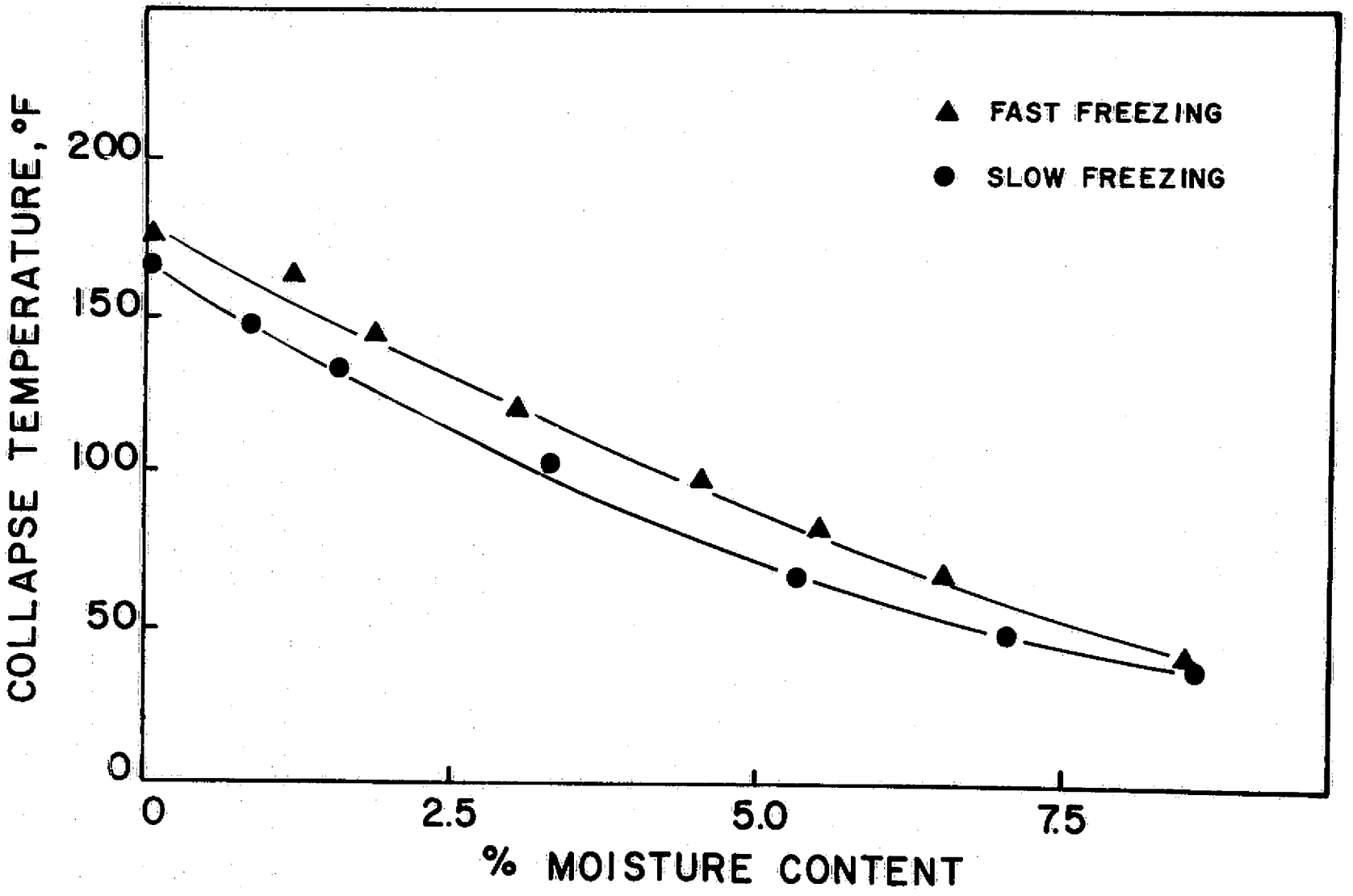
Figure 7 Collapse temperature vs concentration of gum arabic in orange juice.

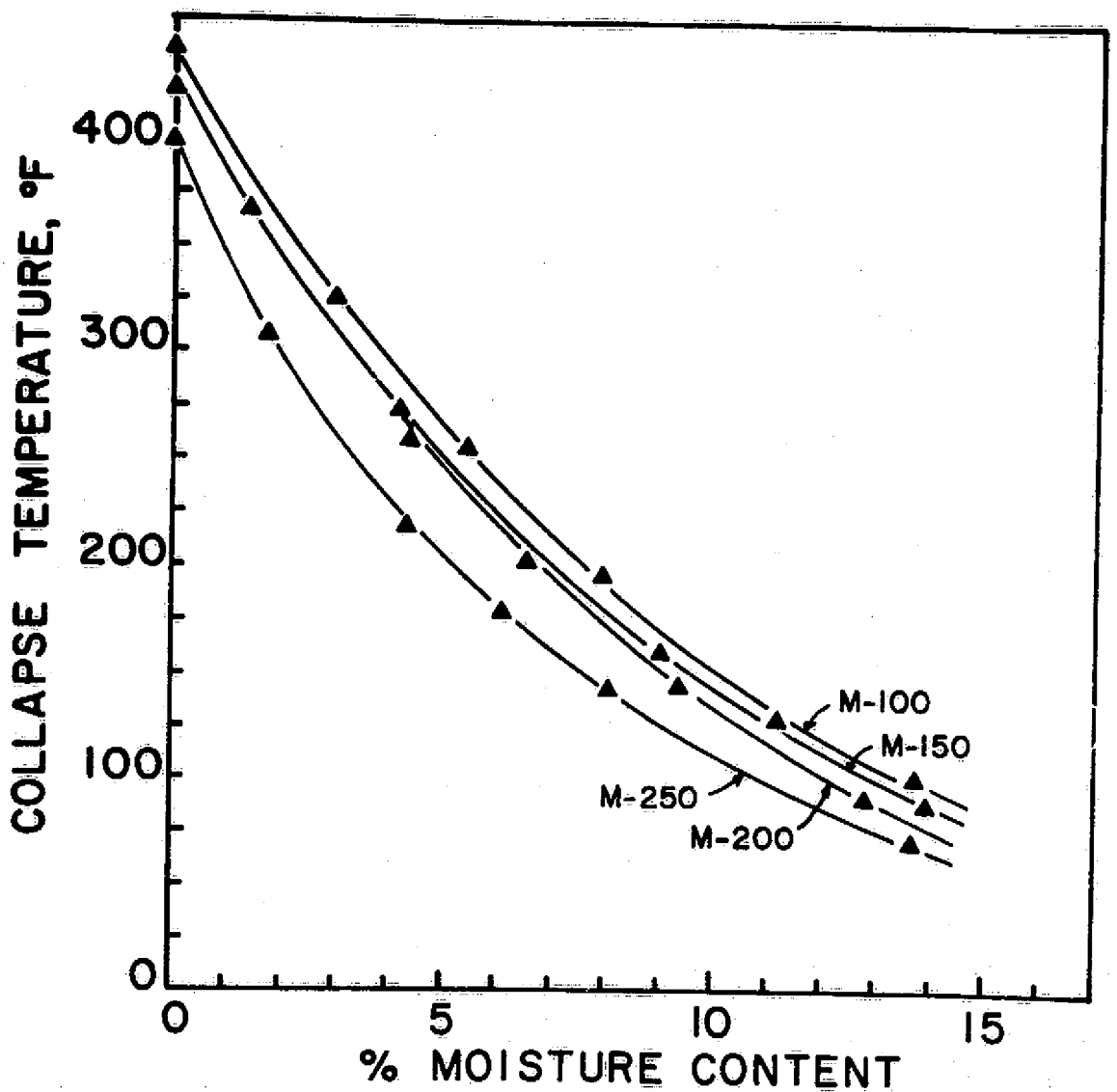
Figure 8 Collapse temeprature vs concentration of tragacanth gum or karaya gum in orange juice.

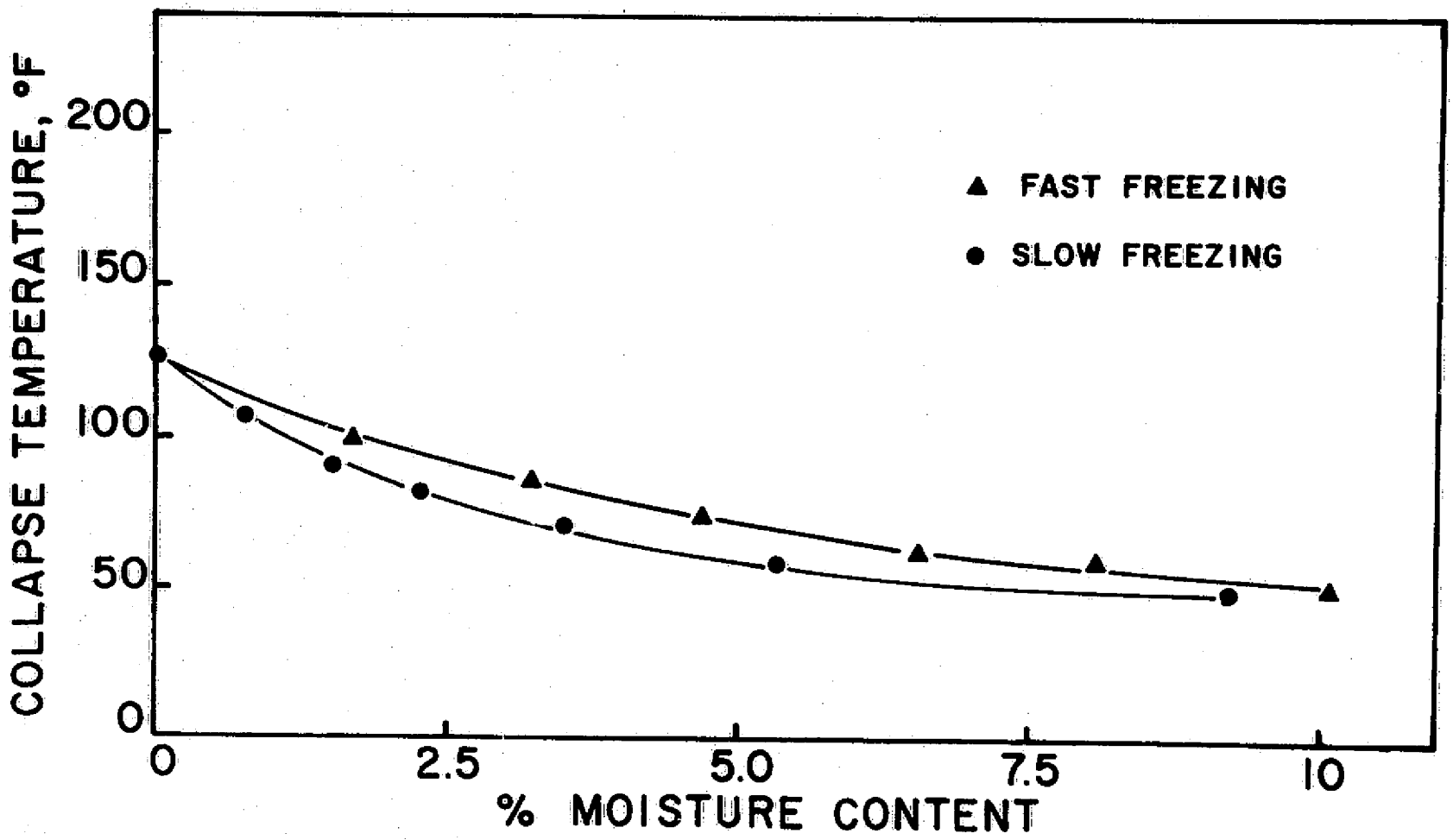
Figure 9 Structural change temperatures vs ln moisture content for collapse during freeze drying, collapse in this work, and sticky point of orange juice powders.

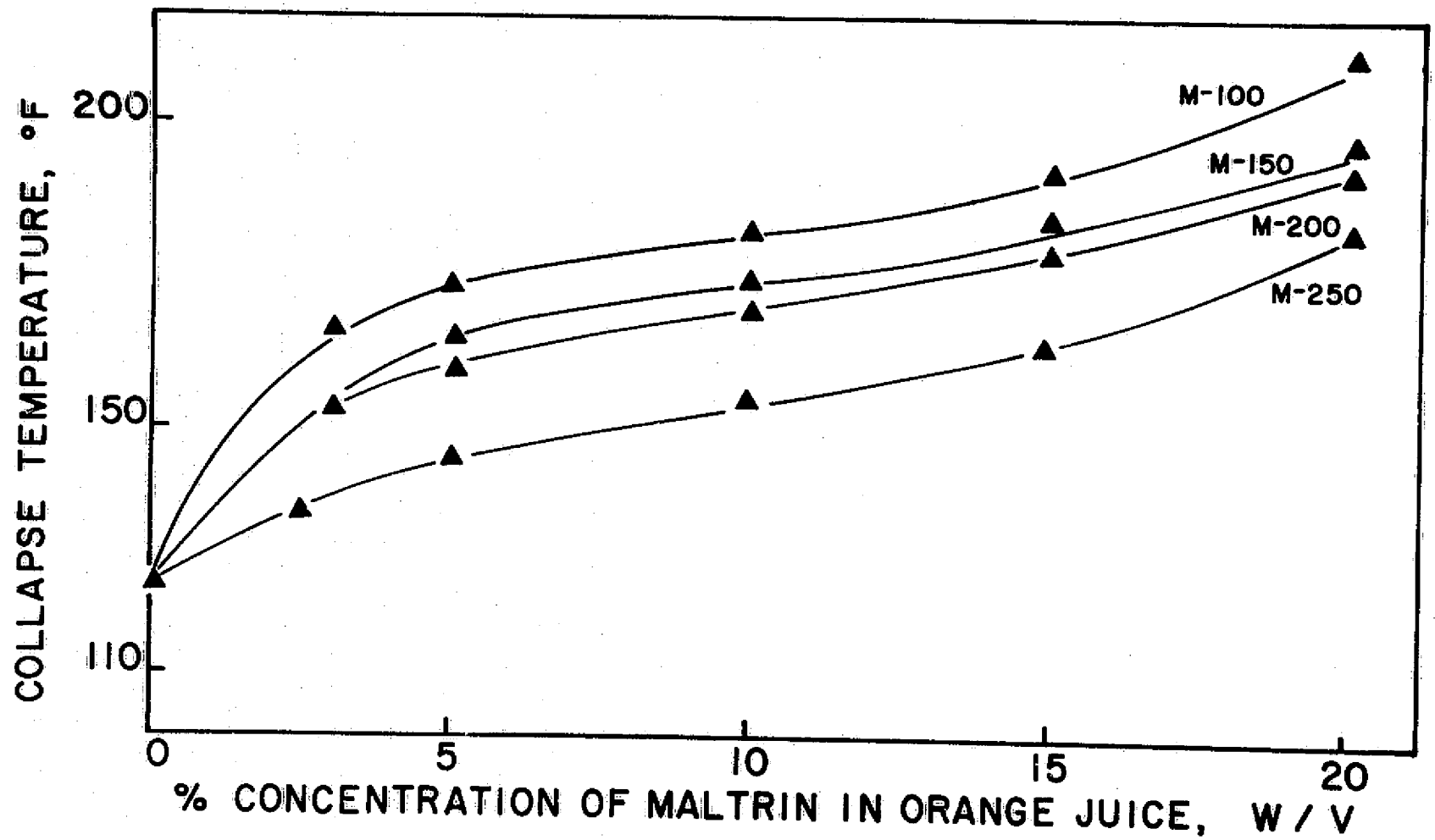

COLLAPSE TEMPERATURE, °F
100
120
140
160
0
50
100
TIME, MINUTES

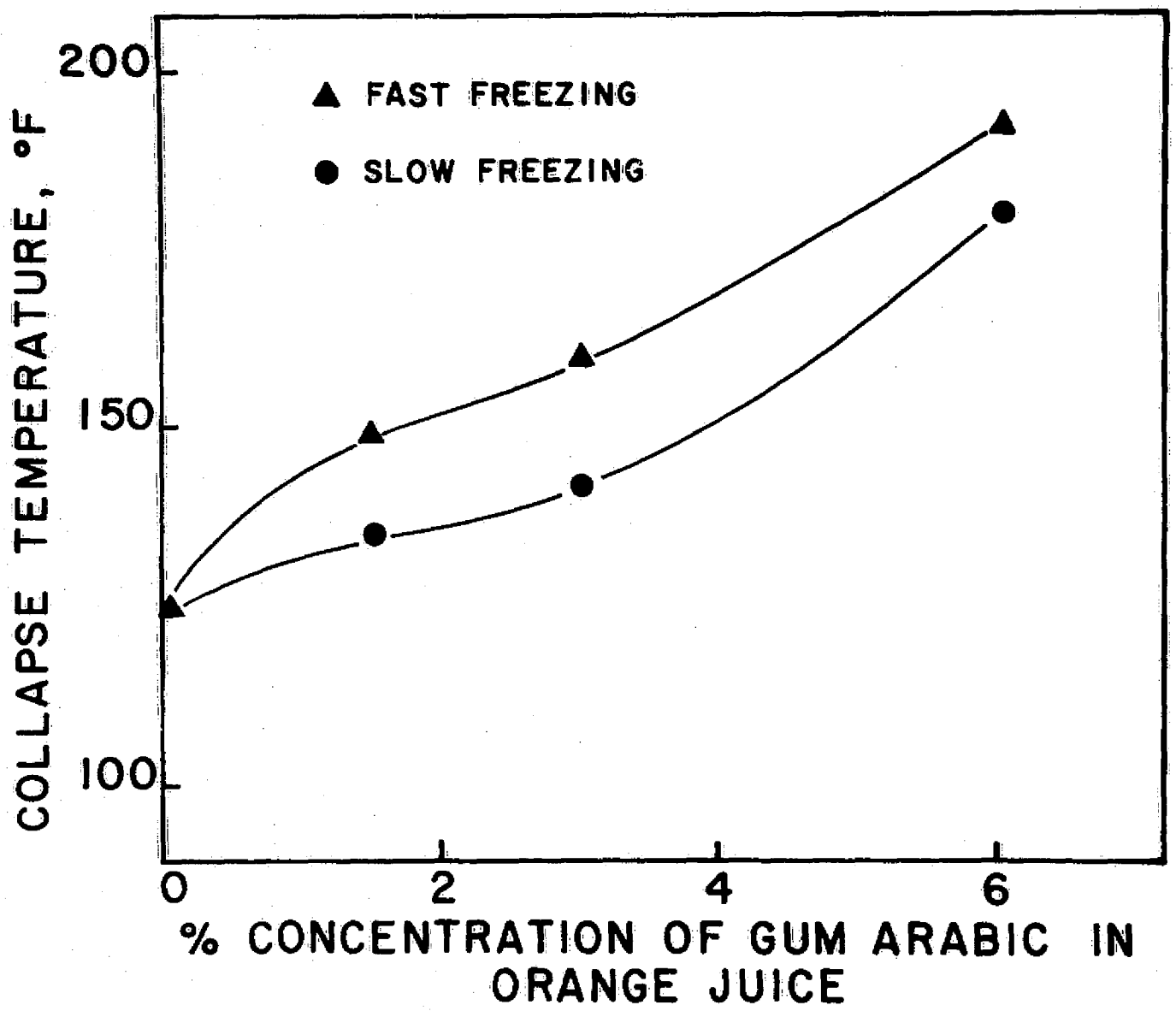

COLLAPSE TEMPERATURE, °F
200
150
100
50
0
0
2.5
5.0
7.5
% MOISTURE CONTENT
FAST FREEZING
SLOW FREEZING

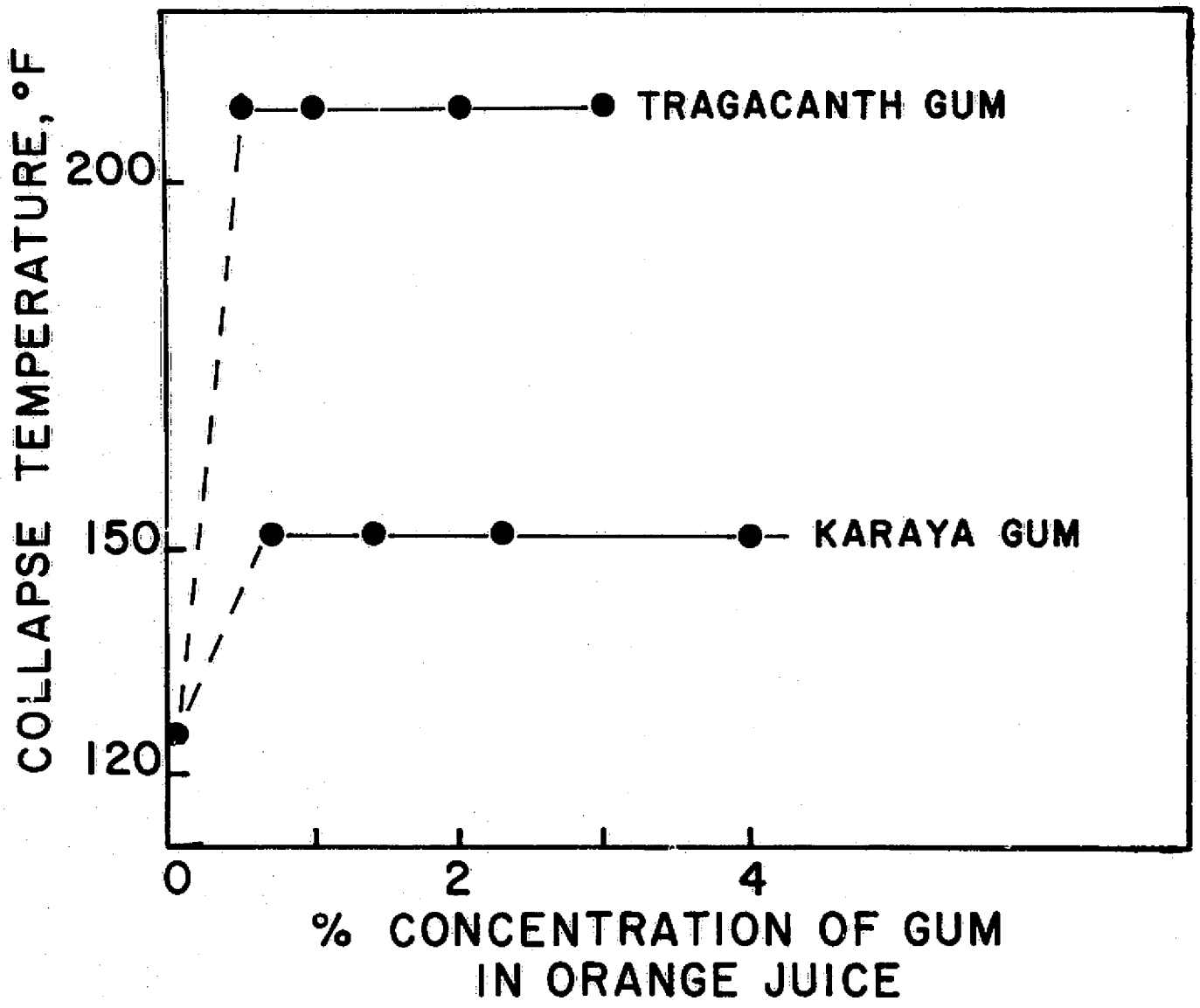

FAST FREEZING
SLOW FREEZING
COLLAPSE TEMPERATURE, °F
200
150
100
50
0
0
2.5
5.0
7.5
% MOISTURE CONTENT

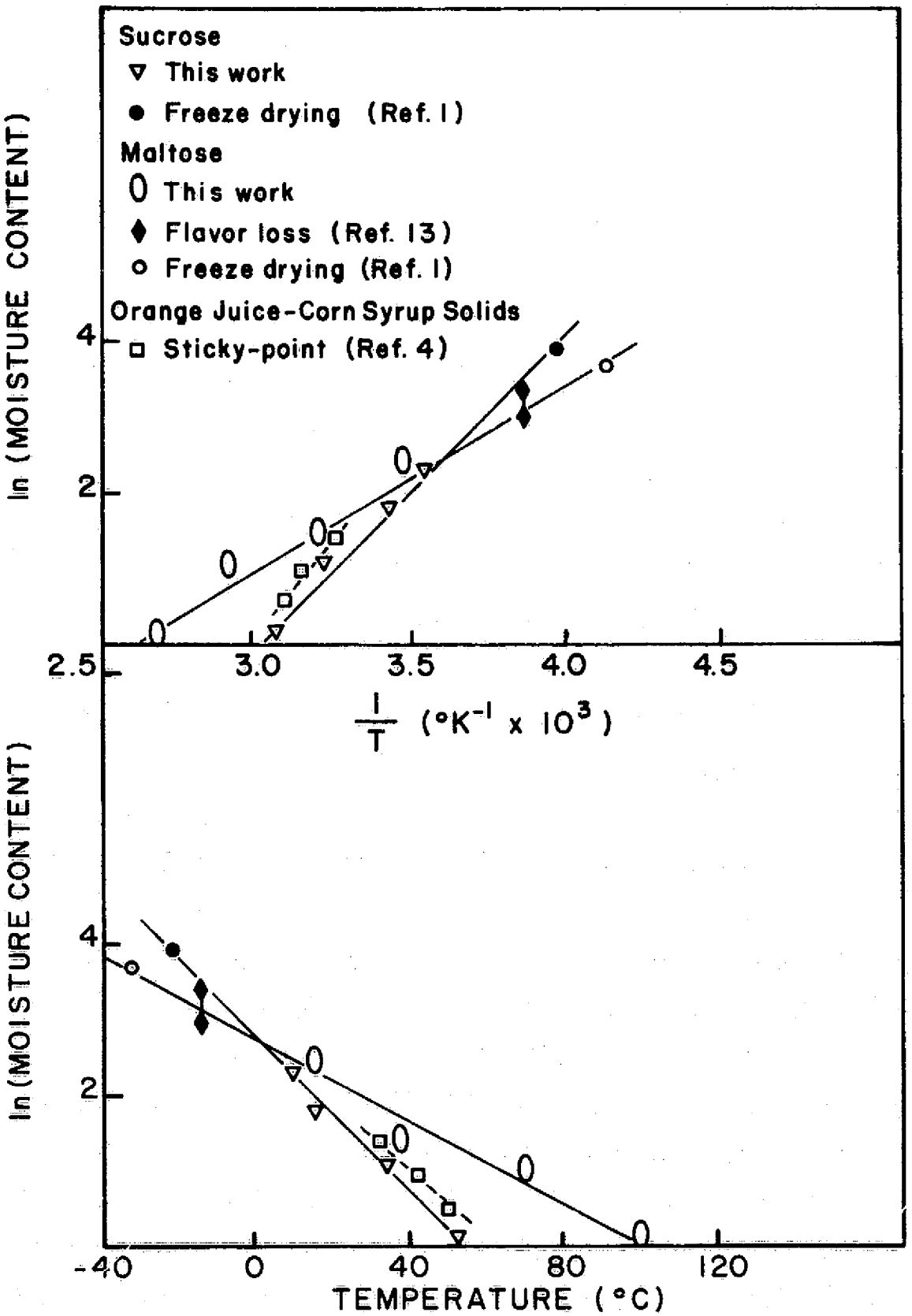

COLLAPSE TEMPERATURE, °F
400
300
200
100
0
0
5
10
15
% MOISTURE CONTENT
M-100
M-150
M-250
M-200


COLLAPSE TEMPERATURE, °F
200
150
100
50
0
0
2.5
5.0
7.5
10
% MOISTURE CONTENT
▲ FAST FREEZING
● SLOW FREEZING


COLLAPSE TEMPERATURE, °F
200
150
110
0
5
10
15
20
% CONCENTRATION OF MALTRIN IN ORANGE JUICE, W / V
M-100
M-150
M-200
M-250


200
150
100
COLLAPSE TEMPERATURE, °F
▲ FAST FREEZING
● SLOW FREEZING
0
2
4
6
% CONCENTRATION OF GUM ARABIC IN ORANGE JUICE


COLLAPSE TEMPERATURE, °F
200
150
120
0
2
4
% CONCENTRATION OF GUM
IN ORANGE JUICE
TRAGACANTH GUM
KARAYA GUM


Sucrose
This work
Freeze drying (Ref. 1)
Maltose
This work
Flavor loss (Ref. 13)
Freeze drying (Ref. 1)
Orange Juice-Corn Syrup Solids
Sticky-point (Ref. 4)
ln (MOISTURE CONTENT)
4
2
2.5
3.0
3.5
4.0
4.5
1/T (°K⁻¹ x 10³)
ln (MOISTURE CONTENT)
4
2
-40
0
40
80
120
TEMPERATURE (°C)

4. Artificial Food Matrices (AFM)

4.1 Introduction

Work has continued on gel systems which simulate fruits and which are capable of preservation by freezing and/or freeze drying without loss of desirable organoleptic quality. Methods for incorporation of typical water and lipid-soluble micro-nutrients (vitamins) were investigated during Phase IV. The major effort in the area of artificial food matrices has concentrated on characterization of the mechanical properties of the gel systems in order to develop techniques for predicting the influence of composition and process variables on texture fabrication and modification for producing new engineered AFM systems of improved quality.

4.2 Fabrication of Artificial Food Matrices

The methodology for fabrication of the AFM, some properties of the products and evaluations of organoleptic quality of AFM incorporated in various food systems are given in the following technical article entitled "A Simulated Fruit Gel Suitable for Freeze Dehydration". This article has been published in the Journal of Food Science.

Reprinted from Journal of Food Science.
© 1976 by Institute of Food Technologists.

NANCY LUH, MARCUS KAREL and JAMES M. FLINK
Dept. of Nutrition & Food Science, Massachusetts Institute of Technology, Cambridge, MA 02139

ORIGINAL PAGE IS
OF POOR QUALITY

A SIMULATED FRUIT GEL SUITABLE FOR FREEZE DEHYDRATION

ABSTRACT

Acceptance of new food resources may be achieved by simulation of traditional foods. Sodium alginate gels may be used to produce a desirable fruit-like texture useful as a base for fabricated nutrient-controlled foods. A two-step gelation process has been used to produce fruit-like textured products. These products can be flavored as desired and utilized without further processing to simulate fresh fruit pieces, or they may be either frozen and thawed, or freeze dried and rehydrated without loss of desirable texture. The freeze-dried materials rehydrate rapidly and when incorporated into food products such as yogurt, the rehydrated material compares favorably with rehydrated freeze-dried fruits or currently available commercial fruit yogurts.

INTRODUCTION

ACCEPTANCE of new food resources may be achieved by simulation of traditional foods through food analogs. In the field of food analog fabrication, most attention has been focused on protein-based food products (Inglett, 1975). Less work has been done on simulated fruits or vegetables, and less still regarding the processing stability and properties of simulated fruits and vegetables. Studies on the molecular basis of structural properties of fabricated foods have also focused on proteins (Stanley et al., 1972; Cumming et al., 1972; Buttkus, 1974).

Szczesniak (1968) showed that nonuniform cellular structures which simulate fruits and vegetables may be prepared by dialyzing certain alkaline earth metal salts, such as the acid salts of calcium or magnesium, at a uniform rate into an aqueous solution of water soluble alginate salt of suitable viscosity and concentration. Rapp and Ziemba (1972) employed corn syrup, invert sugars, carrageenan, color and flavor to produce structured, colored and flavored bits as ready-to-use replacements for fruits and confections in frozen and baked goods. A method of preparing a fruit product having a nonuniform texture simulating that of soft fruits has been developed by Wood et al. (1974). In this process drops of fruit pulp or puree incorporating dissolved calcium or aluminum ions is brought into contact with an alginate or pectate solution to form the "skin" of the fruit. Recently also a series of papers has been published by Russian workers who have used polysaccharides and/or proteins to produce textured systems. Alginate gels as well as gelatin-polysaccharide gel systems were used in these studies, which resulted in formation of anisotropic gels simulating various food products (Tolstogusov, 1974). The delicate texture of fruits or simulated fruit systems usually cannot sustain freeze drying treatment, becoming either spongy or rubbery after rehydration. The development of a method for producing a food matrix system which simulates fruit texture with good sensory quality and processing stability is reported here. In addition, some properties of the food matrix system are also noted.

EXPERIMENTAL

Gel formation and preparation

Development of formulation. The materials used for these studies were sodium alginate (Kelco Gel LV, KGLV 2475-52, Kelco Co.), calcium lactate (N.F. Powder, Mallinckrodt Chemical Works), citrus pectin (Sigma Chemical Co.), gelatin (Knox unflavored gelatin), Avicel and sucrose.

Initial tests with controlled interaction of sodium alginate (water soluble alginate salt) and calcium lactate (source of calcium ions) produced calcium alginate gels which had a crisp cucumber-like texture. However, after a freeze-thaw cycle, a product with undesirable rubbery and spongy texture was obtained. Another defect of the simple calcium alginate system was the poor breakdown properties of the gel toward the end of mastication. While the product had the cucumber-like crisp texture on the first bite, upon further chewing it became progressively drier rather than maintaining juiciness like natural cucumber. It was also somewhat unpleasant to swallow. To improve the sensory quality of the calcium alginate gel upon chewing, compounds of high water holding capacity were incorporated. These included dextran, starch, sucrose and pectin, tried either singly or in combinations.

The addition of pectin and sucrose to the alginate solution prior to the crosslinking process resulted in a gel with improved chewing quality. Pectin can absorb large quantities of water which is probably the main reason for its effectiveness.

Gelatin was added to the sample mixture when the two-step gelation procedure was developed. The gelatin allows the system to be thermally gelled prior to the chemical crosslinking with calcium ions.

In order to minimize textural damage due to mechanical forces exerted by the expanding ice crystals during freezing, the following procedures were adopted.

Avicel, a water insoluble microcrystalline cellulose was incorporated to create nucleation sites thus increasing their number and decreasing the size of ice crystals. The crosslinked matrix was also partially dehydrated prior to freezing either by air drying or an osmosis treatment against a 50% sucrose solution. The water content was reduced by 20–30% prior to freezing. With the addition of these procedures the freeze-thawed matrices were no longer cracked into pieces, nor were mushy, but instead, had a texture almost equal to the fresh matrices.

When this system was tested for retention of desirable texture following freeze drying and rehydration, a variable degree of success was achieved. For some samples good texture retention was found, while in others, the texture was significantly degraded. Comparative organoleptic evaluations showed that changes in texture noted in rehydrated samples were due mainly to changes which occurred during freeze drying or rehydration. If the matrix had collapsed during freeze drying a poor quality product was invariably obtained. Collapse also affected the appearance of the freeze dried matrices, and increased the rehydration time significantly.

A number of possible causes for this collapse phenomenon could be identified:

(1) High sucrose concentration due to sucrose incorporated initially in the matrix system;

(2) Collapse of one or more of the matrix polymeric components;

(3) Reduced mass transfer due to surface sucrose sorbed by the matrix during osmosis; and

(4) Partial melting of the frozen matrix during freeze drying.

A series of experiments showed that all these factors except collapse of the macromolecular matrix components had some influence. Most critical was an apparent melting during the early stages of freeze drying. Melting could be reduced or prevented by chilling the frozen samples in liquid nitrogen prior to insertion in the freeze dryer, and/or by precooling the freeze dryer plates for the initial drying period. The rate of freezing also played an important role, with rapid freezing giving somewhat increased collapse of the structure when compared to identically treated samples which had been slowly frozen.

The calcium alginate gel which could be successfully frozen and

thawed without loss of texture could also be successfully freeze dried and rehydrated without changing composition, if the freeze drying process was conducted so as to prevent matrix collapse. In general, this involved slow freezing and insuring that the sample was well chilled during the initial stage of freeze drying.

Matrix formation procedures

Initial studies were conducted using a mold and membrane system to contain the alginate solution during a one-step gelation procedure. This led to a number of difficulties especially because of a long gelation time, and a two-step gelation procedure has been developed. The crosslinking reaction resulting from controlled diffusive contact of the sodium alginate mixture with calcium ions from the calcium lactate solution is now preceded by a thermal gelation step. System preparation involves chilling the gelatin-containing alginate mixture at refrigeration temperatures to obtain a soft gelatin gel. The minimum concentration of gelatin which is required to preshape the alginate mixture is 1.5% (w/w). It appears that at this concentration gelatin does not interfere with the subsequent crosslinking of the alginate. The soft gelatin gel is sliced and then placed directly into calcium lactate solution at room temperature for sufficient time to completely crosslink the alginate. The time required for matrix formation using this two-step gelling procedure depends on the size of the soft gelatin slices, which can be varied easily according to needs.

Textural quality of the fresh matrix as determined by a three person panel was satisfactory, being equal to the better quality samples obtained earlier with the nonthermally pre-gelled process.

Advantages of the two-step gelation procedure over the one-step crosslinking are:

(1) Time required for matrix formation is greatly reduced.

(2) Simplified preparation, as no molds and nylon membrane needed.

(3) Increased flexibility, since the size and shape of the final matrix can be easily varied according to needs instead of being limited by the size and shape of the molds used.

In addition, the two-step gelation procedure simplifies scale up of the production of the matrices.

RESULTS & DISCUSSION

Rate of matrix formation

The formation of the matrix from sodium alginate and calcium lactate occurs through crosslinking of calcium ions with carboxylic groups of the alginate molecules. In order to get a successful gel, calcium ions have to diffuse slowly into the alginate solution. The rate at which this matrix forms in the thermally gelled system was studied by observing the time dependence of the thickness of the cross-linked region. This region can easily be differentiated visually since the thermal gel has a soft consistency which becomes firm after the formation of crosslinks. When the shortest dimension of a three dimensional matrix piece has been fully crosslinked, the crosslinking step is regarded as complete.

The time required for complete crosslinking of a given size of matrix is related to the length of the shortest dimension by

$$t = k\,d^2 \qquad (1)$$

where t is time in minutes, d is one-half of the shortest dimension in centimeters, and k is a constant, which is a function of sample composition, calcium ion concentration and temperature, and is equal to the reciprocal of the diffusion coefficient (d) using the unidirectional Fickian model with the usual simplifying assumptions (Treybal, 1955).

Alginate solutions containing pectin (2%), gelatin (1.5%), Avicel (0.25%) and sucrose (20%) were tested in a calcium lactate bath of 4.5% at alginate concentrations of 1.0—3.0%. An alginate concentration of 1.0% produced a matrix which was not firm enough for measurements to be made.

With alginate concentrations from 1.5—3.0%, there was no observable difference in rate of crosslink formation which was expressible as

$$t = 820\,d^2 \qquad (2)$$

This value corresponds to a value of D of 1.2×10^{-3} cm^2/min (2×10^{-5} cm^2/sec), which is in the range of expected values for diffusion of electrolytes in water and food gels (Karel, 1975).

The influence of calcium ion concentration on rate of matrix formation is shown in Figure 1 for an alginate solution of 2.5% alginate, 2.0% pectin, 1.5% gelatin, 0.25% Avicel and 20% sucrose. These rates can be expressed by the following equations:

$t = 1{,}520\,d^2$	when	$[Ca^{++}] = 1.5\%$
$t = 1{,}120\,d^2$		$[Ca^{++}] = 3.0\%$
$t = 820\,d^2$		$[Ca^{++}] = 4.5\%$

Alteration of the sucrose concentration also influences the rate of matrix formation (Fig. 2) when the concentration reaches levels above 20%. The retardation of crosslink formation due to sucrose can be expressed by:

$t = 768\,d^2$	when	sucrose = 0%
$t = 821\,d^2$		sucrose = 20%
$t = 1{,}150\,d^2$		sucrose = 30%

The influence of calcium ion concentration gradient and sucrose concentration on the rate of matrix formation suggests that the rate of matrix formation is controlled by the rate of diffusion of calcium ions, which is independent of alginate concentrations in the ranges used.

Properties of the food matrix

Structure. The matrix microstructure was investigated using optical and scanning electron microscope techniques.

Grains of the freeze-dried fabricated food matrix were examined using the optical microscope. When immersed in oil and examined at 600 x magnification, the grains appeared

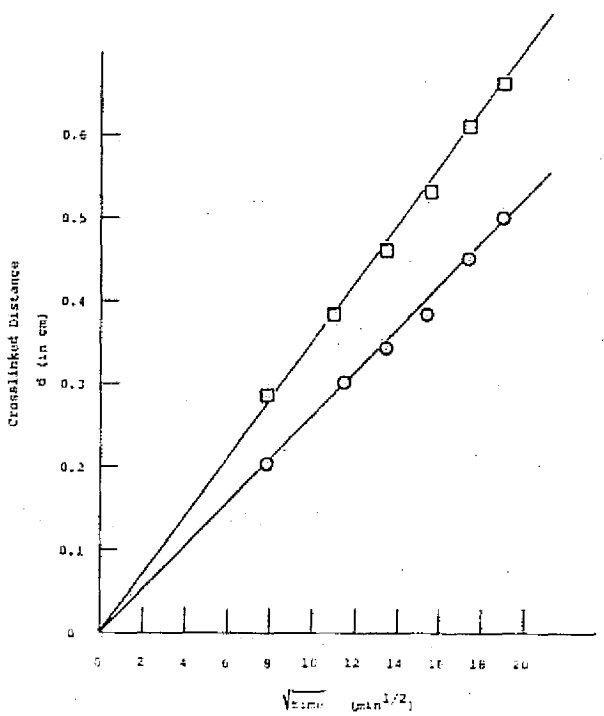


Fig. 1—Effect of calcium ion concentration on the rate of matrix formation: ○ Calcium lactate 1.5% (w/w); □ Calcium lactate 4.5% (w/w).

homogeneous. However when crossed polarizers were used, anisotropic regions were clearly distinguished from the remainder of the grain. When water was added, swelling of the grain was observed, and the Avicel microcrystals which will not dissolve or swell in water, were seen to be dislocated by the swelling of the food matrix. The strongly anisotropic regions remained following the rehydration. It can be assumed therefore that these regions are Avicel, since any sucrose crystals would disappear after rehydration.

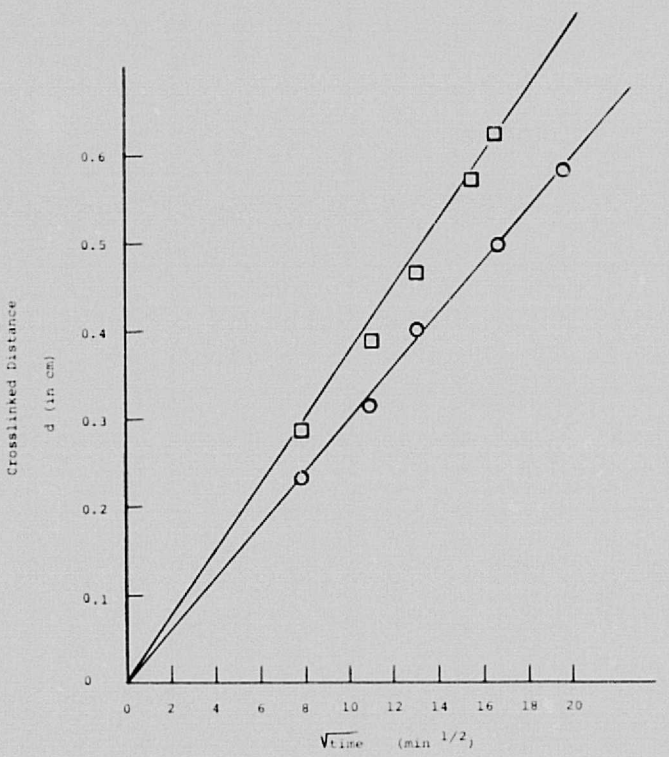


Fig. 2—Effect of sucrose concentration on the rate of matrix formation: ○ Sucrose 30% (w/w); □ Sucrose 0%.

A weak anisotropy of the food matrix which decreases upon rehydration and returns after re-evaporation of water was also observed. This appears to be due to a certain degree of polymeric alignment in the dried crosslinked matrix.

Scanning electron micrographs of the surface structure of food matrices which were freeze dried with and without matrix collapse are shown in Figure 3 and 4, respectively. In each sample, many surface pores were observed. However, it can be seen that there is a sizable difference in the size of the pores between collapsed and noncollapsed samples, with the average diameter of noncollapsed samples about tenfold larger than the average diameter of the holes of the collapsed samples. The difference results in an approximately 100-fold difference in the pore cross section area. The two conditions differ therefore very greatly in vapor or liquid flow resistance, and have different structural arrangements of the matrix units which in turn can be expected to alter the overall strength. These factors are probably the reason why the collapsed samples are so tough and hard to rehydrate.

Rehydration. Rehydration behavior of freeze-dried food matrices was studied by measuring weight gain after fixed times of rehydration. To measure sucrose loss during rehydration the dry matrix weight before and after rehydration (i.e., re-freeze dried) was determined.

Percent (%) rehydration compares the weight of water per unit weight of solids after rehydration to the weight of water per unit weight of solids of the product after the osmotic treatment. This can be expressed as

$$\% \text{ Rehydration} = \frac{\frac{w_3 - w_4}{w_4}}{\frac{w_1 - w_2}{w_2}} \times 100$$

where all weights are for a given sample after the indicated treatment: w_1 = weight after osmotic treatment; w_2 = weight of osmotically treated sample after freeze drying; w_3 = weight after rehydration; and w_4 = weight of rehydrated sample after re-freeze drying. It was noted that samples having different pretreatments showed differing rehydration behavior. During rehydration fast and slowly frozen osmotically treated samples

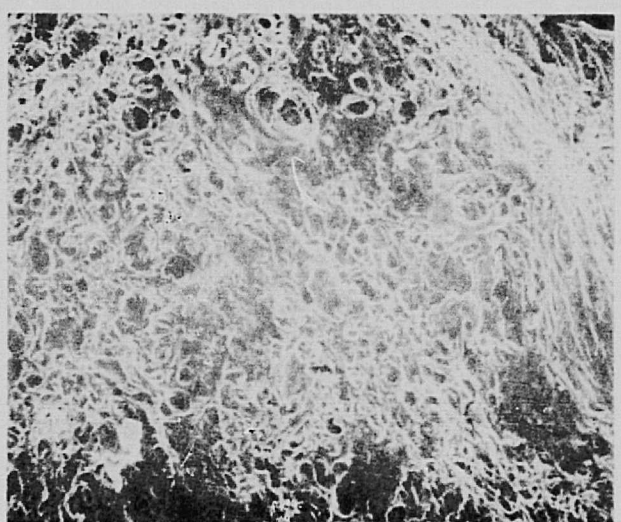


Fig. 3—Surface structure of freeze-dried food matrix as viewed by scanning electron microscope (Collapsed sample—100X).

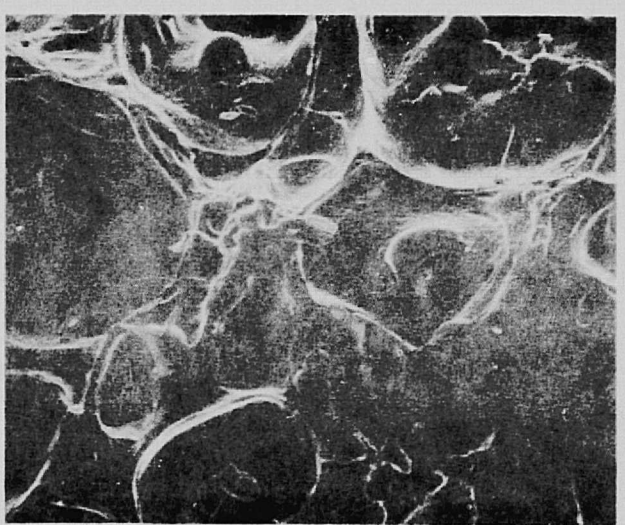


Fig. 4—Surface structure of the freeze-dried food matrix as viewed by scanning electron microscope (Uncollapsed sample—100X).

ORIGINAL PAGE IS
OF POOR QUALITY

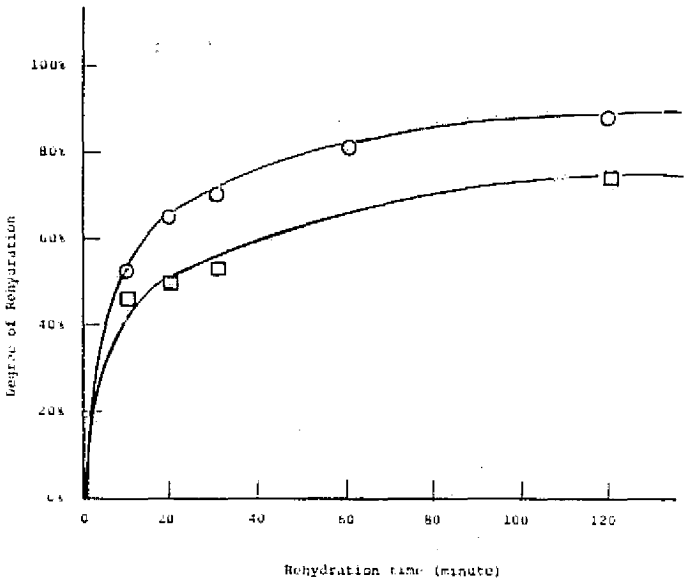


Fig. 5—Rehydration of freeze-dried food matrix (with osmosis treatment): ○ Slow freezing; □ Fast freezing.

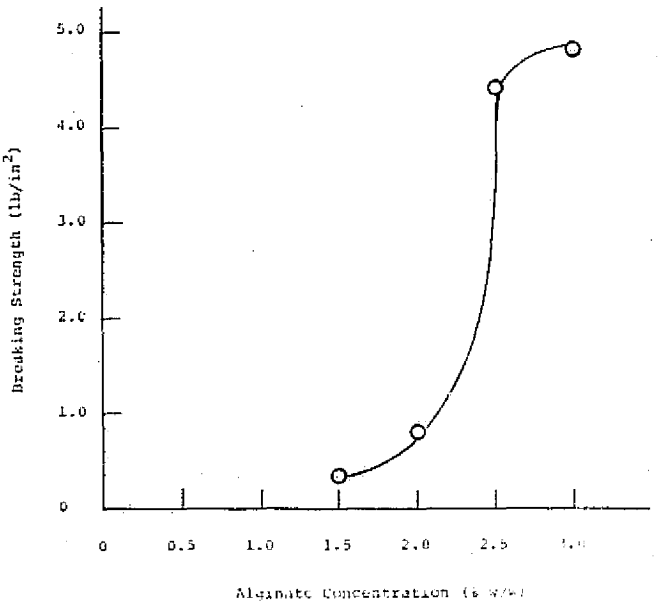


Fig. 6—Effect of alginate concentration on the breaking strengths of the fabricated food matrix.

showed similar loss of sucrose (41 and 45% of the initial sucrose, respectively) while the nonosmotically treated samples showed some differences (54% loss of sucrose for slowly frozen vs 33% loss for fast frozen). In Figure 5 it is seen that a slow freezing prior to freeze drying resulted in samples with a higher rehydration rate than samples rapidly frozen. It was also noted that samples without osmosis treatment rehydrated faster than samples with osmosis treatment. For example after 30 min rehydration osmotically treated samples showed a rehydration of 53% while samples without osmotic treatment had 71%.

Rheology. Changes of rheological properties of the food matrix system brought about by different processing procedures have been evaluated using the Instron Universal Testing Machine. At present any relationship or organoleptic evaluations of texture with rheological properties of the fabricated food matrix is limited in scope and the reported evaluation serve primarily to indicate the influence of process and composition variations on mechanical properties of the matrix. The changes of matrix breaking strength at different alginate concentrations are shown in Figure 6. It is seen that at alginate concentrations lower than 2.0%, the crosslinking is not extensive enough to give a sufficiently strong three-dimensional network, resulting in soft, weak matrices which will not sustain further processing.

Figure 7 shows changes of elastic moduli, breaking strengths and fractural energy densities of samples at various stages of the preparation and use process.

It can be seen that the organoleptically desirable final products, fresh matrix (A), freeze-thawed matrix (without osmotic treatment) (B) and rehydrated freeze-dried matrix (with osmotic treatment and no collapse) (E) have similar values for elastic moduli, breaking strengths and fractural energy densities. Freeze-dried and rehydrated samples which have not been osmotically treated have high elastic moduli, breaking strengths and fractural energy densities, probably due to rearrangement of the macromolecular components of the food matrix which occurred during freeze drying which causes increased stiffness and toughness of the rehydrated samples. Osmotically treated samples freeze dried without shelf refrigeration during the first period of freeze drying, differed in physical properties from the same sample freeze dried with shelf refrigeration. Partial melting and collapse probably gives a more dense, rigid structure, resulting in the much higher elastic modulus, breaking strength and fractural energy density. Samples prepared with 30% sucrose in the initial alginate mixture show much smaller variation in rheological properties than

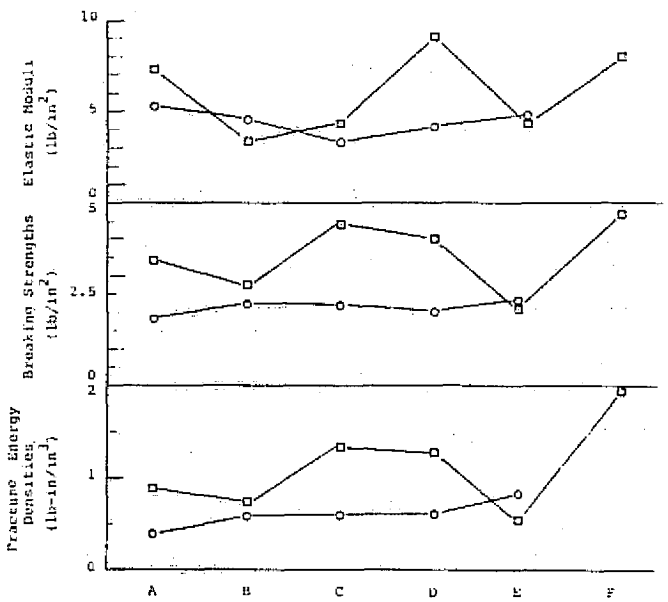


Fig. 7—Effect of processing on the rheological properties of fabricated food matrices: (A) Fresh samples; (B) Frozen-thawed samples; (C) Frozen-thawed samples (with osmosis treatment); (D) Freeze-dried and rehydrated samples; (E) Freeze-dried and rehydrated samples (with osmosis treatment); (F) Freeze-dried and rehydrated sample (with osmosis treatment, partially collapsed): ○ 30% Sucrose; □ 0% Sucrose.

Table 1—Organoleptic scores for products containing food matrices

Product	Number of panelists	Organoleptic score: Taste $\bar{x}$[b]	Taste σ[c]	Texture $\bar{x}$	Texture σ	Ranking[a]: Rank	Ranking $\bar{x}$	Ranking σ
Peach Yogurt								
Yogurt with food matrices[d]		4.36	1.21	3.70	1.57	2	−0.08	0.60
Yogurt with freeze-dried fruit[e]	11	3.82	1.17	4.10	1.37	3	−0.31	0.69
Commercial yogurt[f]		4.64	1.03	4.20	1.23	1	+0.39	0.70
Strawberry Jello								
Jello with food matrices		4.17	1.03	3.83	0.72	2	−0.14	0.71
Jello with freeze-dried fruit	12	4.50	1.00	3.83	1.34	1	+0.28	0.66
Jello with frozen fruit		4.00	1.21	4.17	1.03	2	−0.14	0.71
Pineapple Yogurt								
Yogurt with food matrices		3.42	1.16	4.25	1.14	3	−0.28	0.55
Yogurt with freeze-dried fruit	12	4.42	1.56	4.67	0.98	1	+0.43	0.77
Commercial yogurt		3.92	1.44	4.30	1.37	2	−0.14	0.61
Banana Yogurt								
Yogurt with food matrices		3.46	1.05	3.31	0.95	2	−0.33	0.55
Yogurt with freeze-dried fruit	13	3.62	1.04	3.69	0.85	2	−0.33	0.55
Yogurt with fresh fruit		5.00	0.91	4.62	1.26	1	+0.65	0.51
Pineapple Yogurt								
Yogurt with food matrices		3.92	1.00	3.33	1.23	2	−0.21	0.38
Yogurt with canned fruit	12	5.08	0.67	5.00	0.74	1	+0.71	0.33
Commercial yogurt		2.83	1.11	3.58	1.08	3	−0.50	0.67
Pineapple Yogurt (Evaluated as dry snack)								
Yogurt with food matrices		4.08	1.38	4.00	1.40	1	+0.23	0.80
Yogurt with freeze-dried fruit	12	3.58	1.31	3.83	1.48	2	−0.07	0.74
Commercial yogurt		3.50	1.08	3.83	1.27	3	−0.14	0.57

[a] Values given for ranks are: first (0.81), second (0) and third (−0.81).
[b] $\bar{x}$ = mean.
[c] σ = standard deviation.
[d] Yogurt with food matrices: Plain yogurt with sugar added containing rehydrated food matrices of desired flavor and color.
[e] Yogurt with freeze-dried fruit: Plain yogurt with sugar added containing rehydrated freeze-dried fruit.
[f] Commercial yogurt: Commercial fruit yogurt of desired variety.

those without sucrose included. Sucrose seems to play an important role in stabilizing the texture of the matrix during processing.

Applications of food matrices

Organoleptic evaluations have been conducted on products containing the food matrices as a substitute for fruit products. Comparisons were made with products containing freeze-dried fruits prepared in our laboratory, and to equivalent commercially available products. Organoleptic quality was evaluated using a difference analysis test having a six-point hedonic scale running from excellent (6) to very poor (1) and a ranking preference test with the most preferred first. The results presented in Table 1 are encouraging. Only fresh banana and canned pineapple were rated better than the fabricated food matrices which had been freeze dried and rehydrated.

A number of advantages which result when using the food matrices as fruit substitutes are:

(a) Controllable size and shape which are more uniform than freeze-dried fruits.

(b) No discoloration problems, such as due to enzymatic browning.

(c) When the product is consumed as a dry snack the food matrix is less chewy or sticky to teeth and more crunchy.

The results presented here demonstrate the feasibility of preparation of satisfactory fruit-simulating gels as components of freeze-dried products. The economic value of this approach will depend on future needs for engineered foods with capability for controlling texture and nutrient content.

REFERENCES

Buttkus, H. 1974. On the nature of the chemical and physical bonds which contribute to some structural properties of protein foods: A hypothesis. J. Food Sci. 39: 484.

Cumming, D.B., Stanley, D.W. and deMan, J.M. 1972. Texture-structure relationships in texturized soy protein. 2. Textural properties and ultrastructure of an extruded soybean product. J. Inst. Can. Sci. Technol. 5: 124.

Inglett, G.E. 1975. "Fabricated Foods." Avi Publishing Co., Westport, Conn.

Karel, M. 1975. Properties controlling mass transfer in foods and related model systems. In "Theory Determination and Control of Physical Properties of Food Materials," Ed. Rha, C.K. p. 221. D. Reidel, Dordrecht, Netherlands.

Rapp, H. and Ziemba, J.V. 1972. New way to "dress up" foods. Food Eng. 44(5): 54.

Szczesniak, A.S. 1968. Artificial fruits and vegetables. U.S. Patent 3,363,831.

Stanley, D.W., Cumming, D.B. and deMan, J.M. 1972. Texture-structure relationships in texturized soy protein. 1. Textural properties and ultrastructure of rehydrated spun soy fibers. J. Inst. Can. Sci. Technol. 5: 118.

Tolstogusov, W.B. 1974. Physikochemische Aspekte der Herstellung Künstlicher Nahrungsmittel. Die Nahrung 18: 523.

Treybal, R.E. 1955. "Mass-Transfer Operations," Ch. 4. McGraw-Hill, New York.

Wood, F.W., Woods, M.F. and Young, R. 1974. Food products of non-uniform texture. Canadian Patent 944,604.

Ms received 6/11/75; revised 8/7/75; accepted 8/11/75.

Presented at the 35th Annual Meeting of the Institute of Food Technologists, Chicago, Ill., June 9—12, 1975.

The authors gratefully acknowledge the support of this work by NASA/JSC No. NAS 9-12485.

4.3 Studies on Micronutrient Incorporation

The ultimate AFM would be solid food pieces of desired texture whose nutrient composition can be completely specified. As described in the previous section (4.2), the technology for preparing AFM of desirable textrual qualities has been developed in the course of this contract. In Phase IV, techniques for incorporation of a typical lipid soluble vitamin (β-carotene, i.e. Vitamin A activity) and a typical water soluble vitamin (Vitamin C) have been investigated.

4.3.1 β-carotene incorporation

To incorporate lipid soluble materials at low concentrations in the AFM, it is desirable to have a lipid phase present in which these materials may be solubilized.

Initial tests were therefore conducted on the effect of incorporation of lipid on the process and on the artificial food matrix properties. At phase volumes up to 2% (based on the wet matrix), there was no apparent effect of the lipid on the textural properties of the food matrix. Tests with dyed lipids and with OsO_4 staining have shown that no lipid is lost from the thermally stabilized gel during the time that crosslinking is taking place in the calcium lactate bath. Incorporation of lipid-soluble vitamins were thereafter accomplished by preparing emulsions of oil in the gel solution followed by the thermal gelation and crosslinking reactions.

It was decided to target the incorporation of β-carotene

at a level so that 100 grams of the wet gel contained 10% RDA of Vitamin A. The RDA for Vitamin A is 5000 IU and since 1 IU equals 0.6 microgram of β-carotene, it is necessary to add 0.3 mg β-carotene per 100 grams of wet gel. Sufficient β-carotene was dissolved in the oil prior to preparing the oil-in-gel emulsion. The recovery of the β-carotene at the various process steps has been determined spectrophotometrically by reading the absorption of an extract at 436 nm and comparing the reading to a standard curve of β-carotene. The recovery from the gelatin gel is about 66% of that added to the initial solution (0.3 mg/100g wet gel). During the residence in the calcium lactate crosslinking bath there is further loss to a level which is 46% of the initial value. Freeze drying causes very little additional loss and at the end of the process 45% of the β-carotene has been retained.

The low retention of β-carotene after thermal gelation and crosslinking could be due to a number of factors:

a) Prior to emulsification, it has been necessary to use high temperatures to prepare the gelatin solution. The gelatin solution, with added alginate, pectin and sucrose was maintained at elevated temperature to give reduced viscosity during emulsification and to prevent gelling of the gelatin. The emulsification step requires only one minute, but to get a good gelatin gel, the warm solution cannot be cooled too rapidly. This results in some time that the sample is at elevated temperatures during which β-carotene destruction may occur. It might also be noted that during the emulsification step, as presently conducted, air

is probably being incorporated into the liquid. This could enhance the rate of β-carotene degradation.

b) During the residence in the crosslinking bath, which is about 60 hours for the piece sizes used, further degradation of β-carotene can have occurred due to exposure to light as the samples were crosslinked in an open dish at room temperature.

c) During the investigation it has been noted that there exists some difficulties in extracting β-carotene from wet gelatin gels, due to the very viscous slurries which form in the extraction medium. It has not been possible to date to determine if complete extraction of β-carotene has been achieved. Thus the above retention values represent minimum values.

4.3.2 Ascorbic acid incorporation

Tests on incorporation of materials having vitamin C activity at levels of 33% of the RDA/100 grams of wet gel were conducted. The RDA for Vitamin C is 45 mg of ascorbic acid. The initial approach involved dissolving ascorbyl palmitate in the oil phase, in a manner similar to that described above for β-carotene. However, this approach had limited applicability due to the low solubility of ascorbyl palmitate, which prevented incorporation of the desired vitamin C level.

Tests on incorporation of ascorbic acid in the aqueous gel solution prior to thermal gelation or cross-linking were therefore initiated. All tests have been conducted with ascorbic

acid in the cross-linking bath at the same concentration as in the gel to prevent diffusion of the ascorbic acid from the gel. It appears that most of the incorporated ascorbic acid is physically retained in the gel under these conditions. However, the neutral pH of the cross-linking medium renders ascorbic acid unstable and the retention of ascorbic acid after freeze drying has been found to be quite low for this reason.

4.3.3 Conclusion

It appears that micronutrients such as Vitamins can be successfully incorporated into the AFM without significantly affecting the organoleptic quality, though some modifications of the particular process steps will be required.

4.4 Characterization of AFM Texture and Mechanical Properties

4.4.1 The AFM as a Model for Texture Studies of Solid Food

The AFM has been developed as a fruit simulating food material whose nutrient content can be well characterized and reproducibly prepared. In addition to its use as a component of a controlled space food diet, studies related to developing the desired organoleptic textural qualities has indicated an additional unique value of the AFM.

Foods of either plant or animal origin are very complex in composition and structure. Thus it is very difficult to study the relationship between composition and texture using a real food system. The artificial food matrix, however, offers a great

advantage over the real food system in that the composition of the system can be changed at will. These changes include both the alteration of the concentration of each component, or even the presence or absence of a particular component. This makes it possible to develop orderly stepwise studies of the interaction of different components and eventually elucidation of the relationship between composition and texture of food systems. Knowledge obtained from these studies will be very valuable in the future for texture fabrication and modification of engineered food systems.

4.4.2 Static Compression Testing

Studies on rheological properties of the artificial food matrix were conducted using both static loading and dynamic loading devices to measure stress-strain curves. In static load-deformation experiments the deformation of gels after sequential additions of static force was measured by means of a cathetometer.

The effect of crosslinking on the texture of the gel can be seen in Figure 1. By comparing the two curves for the 2.0% alginate systems, it is clear that crosslinked gels are much firmer than noncrosslinked gels. Figure 1 also shows that alginate concentration has an effect on the texture of the crosslinked gels. As the alginate concentration is increased, the firmness of the crosslinked gels also increases.

To find the component(s) making the major contribution to the texture of the crosslinked gels, samples containing pure alginate; alginate with sucrose; alginate with pectin; alginate

with sucrose and pectin; and alginate with sucrose, pectin and gelatin have been prepared and subjected to static compression tests.

The deformation behavior of pure alginate gels was similar to that of gels also containing pectin, gelatin and sucrose (Figure 2). This demonstrates that calcium alginate is the primary contributor to the firm texture of the crosslinked gels, the other components not having a major influence (with the possible exception of gelatin). Changes in pectin concentration modifies somewhat the deformation behavior. However, increases in the amount of pectin above some initial level do not appear to give further increases in the firmness of the gel (Figure 3).

From Figure 2 it is noted that when gelatin was incorporated, the firmness of the crosslinked gels increased. The same phenomenum has also been observed when dynamic compression tests were performed on the crosslinked gels.

4.4.3 Compression testing using the Instron Universal Testing Machine

An Instron Universal Testing Machine Model 1122 has been used to conduct dynamic uniaxial compression tests on cylindrical gel samples. The following test conditions have been used:

a) Crosshead speed: The rheological properties obtained by mechanical tests are dependent on the rate of loading. A crosshead speed of 20 cm/min. is therefore specified.

b) Chart speed: The results of mechanical tests will not be influenced by the chart speed used. However, since the height of the sample is approximately 1.5 cm, and the crosshead speed is 20 cm/min., too slow a chart speed will not reveal the details of the compression behavior of the tested gels. A Chart speed of 50 cm/min was used.

c) Sample size: Constant surface area of the samples (13.81 cm^2) has been used to eliminate possible complications caused by different surface area. There is only small variation of the height of each sample, which is approximately 1.5 cm.

4.4.3.1 Problem of reproducibility

Initially, a petri dish of 15 cm diameter was used for the sample preparation. Thermally set gels were crosslinked with calcium ions diffusing from the top of the gels (the gel was held in the petri dish). When the crosslink reaction was complete, smaller pieces were cut from the large crosslinked gel. Since crosslink formation caused a change of the internal tension of the gel, the center of the large gel sample usually bulged out, and it was impossible to get a flat sample of crosslinked gel. The degree of crosslinking was not equally distributed in a bulged gel, and it was found that samples cut from this kind of gel showed drastically different mechanical properties, depending on the location of the cutting (Table 1).

Sample reproducibility has been improved by using smaller

molds (5.5 cm diameter) to hold the thermally set gels for crosslink reactions. The gels were thermally set in the mold and then the mold was inverted for the crosslinking step with calcium ion diffusion. A heavy load was placed on top of the molds to insure achievement of flat surfaces of the crosslinked gels. The reproducibility of the samples has been improved significantly.

4.4.3.2 Effect of Crosslinking on the Mechanical Properties of the Gels

Figure 4 shows the stress-strain curves of two gels of the same composition, one of which has been crosslinked after the thermal gelation, while the other is the noncrosslinked thermal set gel. The changes in firmness (tangent moduli, i.e., the slope of the stress-strain curve), strength (breaking strength i.e., stress at the breaking point) and toughness (fracture energy density, i.e., total area under the curve) caused by crosslinking are apparent in Table 2 (derived from Figure 4).

4.4.3.3 Effect of gelatin on gel mechanical properties

Figure 5 shows the stress-strain curve of crosslinked alginate gels containing 0% and 2.5% gelatin, respectively. Table 3 shows the effect of gelatin on some of the mechanical properties of the crosslinked gels.

The increased strength and toughness of gelatin-containing crosslinked gels cannot be accounted for by strength and toughness of the gelatin gel alone. Table 4 shows that these

are relatively weak.

4.5 Studies on the role of gelatin in the crosslinked alginate gels

It has been noted above that the gelatin, which has been incorporated to form a soft gel prior to crosslinking, also acts to alter the mechanical properties of the crosslinked gels. This effect cannot be accounted for by the properties of the gelatin gel alone. Three possible causes of mechanical property alteration due to the gelatin incorporation have been investigated.

4.5.1 Interaction of gelatin with the crosslinking agent-calcium lactate

To test if gelatin can interact with calcium lactate to form a more rigid gel, a pure, soft gelatin gel was placed in a calcium lactate solution for 60 hours at room temperature to allow any possible interaction to take place. No evidence of crosslinking was observed after this time. In fact the soft gelatin gel became weaker due to partial dissolution.

4.5.2 Changed rate and pattern of calcium crosslinking due to interference with the diffusion of calcium ions by gelatin

The rate of crosslink formation in 2.5% alginate gels, each containing either 1.5%, 2.0%, 2.5%, or 3.0% gelatin has been studied. The results showed no observable effect of gelatin concentration on the rate of crosslinking in the formation of the calcium alginate gels.

4.5.3 Gelatin acting as a "filler" in the crosslinked calcium alginate network

The rheological literature in material science indicates that the values of mechanical properties such as hardness and strength for mixtures cannot be interpolated from the values of these properties for the contributing phases, because the behavior of each phase depends on the nature of the adjacent phase. For example, a finely dispersed, less ductile particle of a rigid phase inhibits slip and prevents shear of a ductile matrix. Therefore, it is not impossible that the soft gelatin gel, when incorporated with the alginate may enhance the crosslinked calcium alginate to a greater extent than the strength of the gelatin gel itself.

4.5.4 Effect of heat treatments on the mechanical properties of gelatin-containing crosslinked alginate gels

Based on the observation that gelatin alters the mechanical properties of crosslinked alginate gels, it can be expected that the mechanical properties of the gelatin-containing crosslinked gel will be temperature sensitive, since gelatin is a thermal set gel:

$$\text{Gel} \underset{30^\circ\text{C}}{\overset{40^\circ\text{C}}{\rightleftharpoons}} \text{Sol}$$

Compression tests have been conducted on gels heated in water at 200°F for 10 minutes. The tests have been performed either immediately after heating (i.e. while the samples were still hot) or after being cooled in water at room temperature for 6 hours. The stress-strain curves are shown in Figures 6a-6c and the derived mechanical properties are given in Table 5. It can be seen that after heating and cooling, the 2.5% alginate gel became stronger (as evidenced by the higher breaking strength measured, and also increases of the tangent moduli); this may be due to an increased crosslinking density induced by heating.

The changes of weight of gels during heating and cooling and loss of solids due to heating were also measured (Table 6) to determine if the gelatin in the crosslinked gels would be dissolved by heating in water. All gels studied are crosslinked 2.5% alginate gels containing different amounts of gelatin.

Heating resulted in a loss of water from the gel which is irreversible, since soaking the heated gel in water for 6 hours did not increase the moisture content of the gel. Gelatin-containing gels showed thermal plastic behavior upon heating (i.e., they became softer as temperature increased, and tougher again as the temperature decreased). Figure 7 shows the changes of breaking strength of the gels as a function of gelatin concentration at different stages of the heat treatments. It can be seen that when samples containing different concentrations of gelatin were tested while still hot, similar breaking strengths were obtained.

The loss of influence of gelatin at elevated temperature indicates that gelatin behaves as a filler in the crosslinked alginate gels. The association of gelatin and alginate molecules is heat sensitive, since upon cooling, the mechanical strength of the gels was restored.

It was noted that when the gelatin-containing gels were heated in water at 200°F for 10 minutes, no substantial differences in the amount of solids loss was observed indicating that gelatin was not dissolved in the water (Table 6). The gelatin is thus probably either strongly associated with the alginate molecules so as not to be dissolved by water at 200°F, or the alginate matrix is "tight" enough so that gelatin molecules are unable to diffuse through it.

4.5.5 Other Observation

The action of gelatin as a reinforcement of the alginate gels has been discussed above. While the type of crosslinking junction regions differ for alginate and gelatin gels, it would seem reasonable to assume that if gelatin acts to reinforce alginate gels, it would be likely that alginate will reinforce gelatin gels. Table 7 shows some results of the compression tests of gelatin gels containing different amounts of alginate. It can be seen that alginate does reinforce the strength of the thermally set gelatin gels as has been predicted.

In one test the gelatin/alginate mixture was frozen and

crosslinked while still frozen. A very spongy structure was obtained. Upon heating, gelatin was excreted from the spongy structure; a thermal gel surrounding the spongy structure formed upon cooling.

4.6 Texture characterization of some fruits and vegetables

Compression tests have been performed on some fruits and vegetables (Figures 8-12) to develop some values to which the properties of the AFM could be compared. The test conditions used were: a) Crosshead speed : 5 cm/min.

b) Chart speed : 50 cm/min.

Table 8 shows the summary of the mechanical properties of the fruits and vegetable studied, as well as the AFM developed in Phases II and III of this contract, and described in Section 4.2 of this Annual Report.

Table 1

Breaking strengths of some crosslinked gels (showing poor reproducibility due to large sample diameter - see text)

Gelatin (g/100 g)	Breaking Strength (kg/cm^2)
0%	2.14, 1.87, 1.22
1.0%	1.97, 1.12, .86, 1.38
1.5%	2.27, 2.53, 1.15, 1.74
2.5%	3.49, 2.76, 3.16, 2.07

Table 2

Comparisons of mechanical parameters of crosslinked and non-crosslinked gels both containing 1.5% gelatin and 2.5% alginate

Parameters	noncrosslinked gel	crosslinked gel
1. Tangent moduli (kg/cm^2) at strain .2	.2	3.7
.3	.4	10
.4	.55	23
.5	.50	19
2. Breaking strength (kg/cm^2)	.19	6.4
3. Fracture energy density ($kg\text{-}cm/cm^3$)	.04	1.0

Table 3

Effect of incorporated gelatin on the mechanical properties of crosslinked 2.5% alginate gels

Parameters		0% gelatin	2.5% gelatin
1. Tangent moduli (kg/cm^2) at strain	.2	2	2.5
	.3	4	5.5
	.4	7	12
	.5	12	20.5
2. Breaking strengths (kg/cm^2)		5.6	7.4
3. Fracture energy density ($kg\text{-}cm/cm^3$)		.90	1.34

Table 4

Some mechanical properties of thermal set gelatin gels

Parameters		Gelatin concentration (g/100g) 1.5%	2.0%	3.0%
1. Tangent moduli (kg/cm^2) at strain	.2	.10	.10	.10
	.3	.17	.17	.17
	.4	.28	.28	.28
	.5	.44	.58	.83
2. Breaking strength (kg/cm^2)		.12	.16	.33
3. Fracture energy density ($kg\text{-}cm/cm^3$)		2.3×10^{-2}	3.0×10^{-2}	6.7×10^{-2}

Table 5

Influence of Gelatin on Breaking Strength of Heat Treated Alginate Gels

Sample	Average of breaking strength (kg/cm^2)	90% confidence interval of breaking strength[a] (kg/cm^2)	# of samples tested
A) 2.5% alginate			
0% gelatin			
1) Not Heated	5.44	±0.18	10
2) Heated[b]	5.81	±0.26	6
3) Heated & Cooled[c]	7.29	±0.45	6
B) 2.5% alginate			
1.5% gelatin			
1) Not heated	6.71	±0.33	8
2) Heated	5.68	±0.47	5
3) Heated & Cooled	6.84	±0.41	5
C) 2.5% alginate			
2.5% gelatin			
1) Not Heated	7.30	±0.30	8
2) Heated	5.57	±0.28	5
3) Heated & Cooled	7.55	±0.52	6

a) Students' t test used to give 90% confidence interval

b) In water for 10 minutes at 200°F

c) In water for 10 minutes at 200°F followed by 6 hours at room temperature in water.

Table 6

Influence of Gelatin on Weight Changes of Alginate Gels Following Heating and Cooling

Gelatin (g/100g)	Initial Weight (g)	Weight after heating[a]	Weight after cooling[b]	Solid Loss (g)
0	80.28	56.30	57.54	0.89
1.5	79.73	58.20	59.34	1.07
2.5	78.70	63.90	64.24	0.90

a) heated in water of 200°F for 20 minutes

b) cooled in room temperature water for 6 hours

Table 7

Breaking Strength for Alginate Containing Gelatin Gels

Gelatin (g/100g)	Alginate (g/100g)	Average breaking strength (kg/cm^2)	90% Confidence Interval of breaking strength[a] (kg/cm^2)	# of samples tested
1.5	0	0.13	±0.01	6
1.5	2.5	0.17	±0.02	5
2.0	0	0.14	±0.02	4
2.0	2.5	0.24	±0.02	5
3.0	0	0.32	±0.03	5
3.0	2.5	0.42	±0.01	5

a) students' t test was used

Table 8

Mechanical properties of some fruits and vegetables

Item	Tangent moduli (kg/cm^2)	Breaking strength (kg/cm^2)	Fracture energy density ($kg\text{-}cm/cm^3$)
Banana	1.15 - 1.48	.26 - .33	$(4.6 - 7.1) \times 10^{-2}$
Peach	1.48 - 2.63	.20 - .36	$(3.0 - 5.9) \times 10^{-2}$
Cucumber	4.93	.86 - 1.32	1.64×10^{-1}
Apple	12.83	2.04 - 2.73	2.96×10^{-1}
Fruit Simulating gel	0.95	0.71	1.40×10^{-1}

List of Figures

Figure 6c Effect of heat treatments on the stress-strain curve of 2.5% alginate gels containing 2.5% gelatin (crosshead speed 20 cm/min.)

Figure 7 Effect of heat treatment on the breaking strengths of 2.5% alginate gels containing different gelatin concentrations

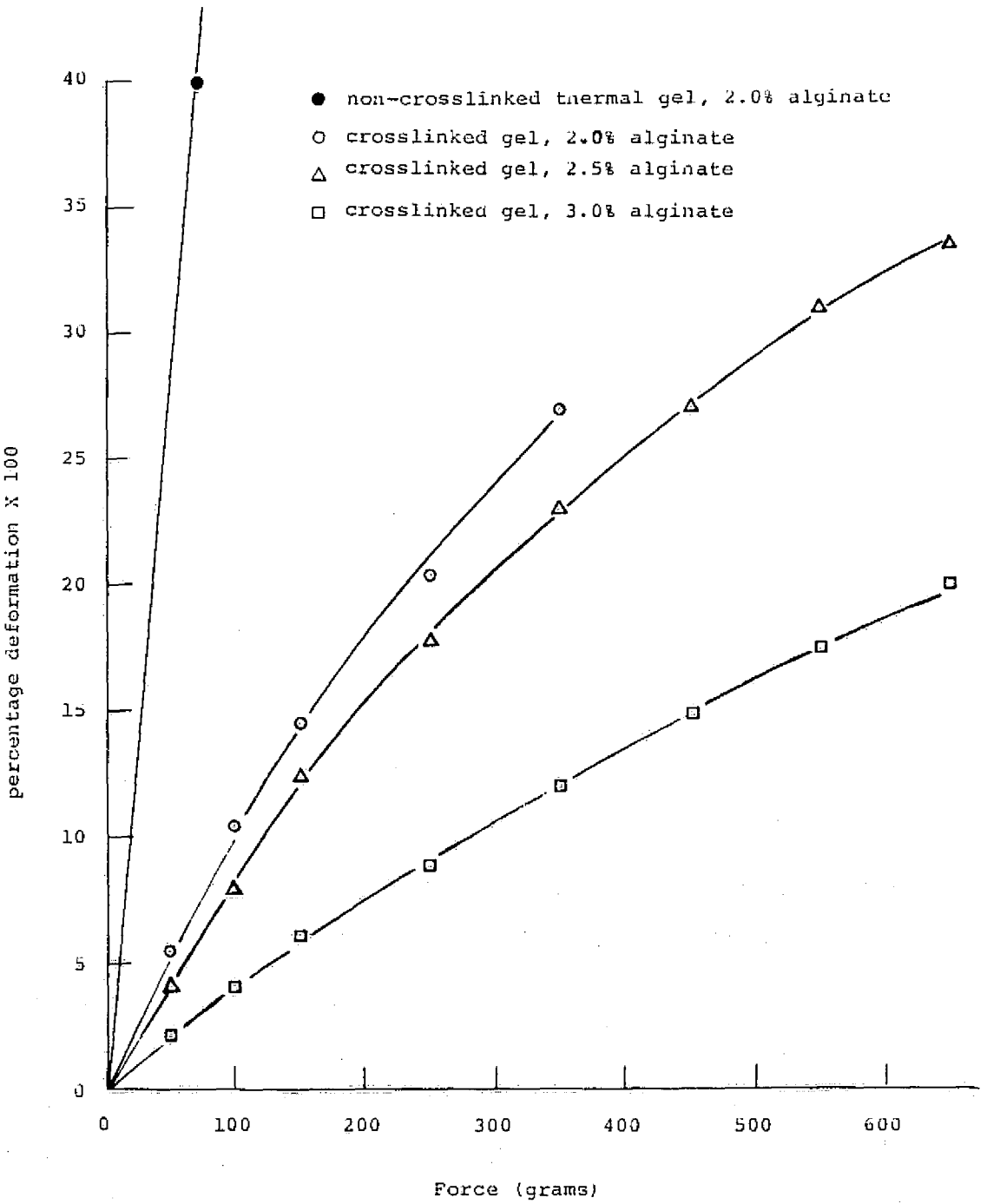
Figure 8 Stress-strain curve of banana under compression loading (crosshead speed 5 cm/min.)

Figure 9 Stress-strain curve of peach under compression loading (crosshead speed 5 cm/min.)

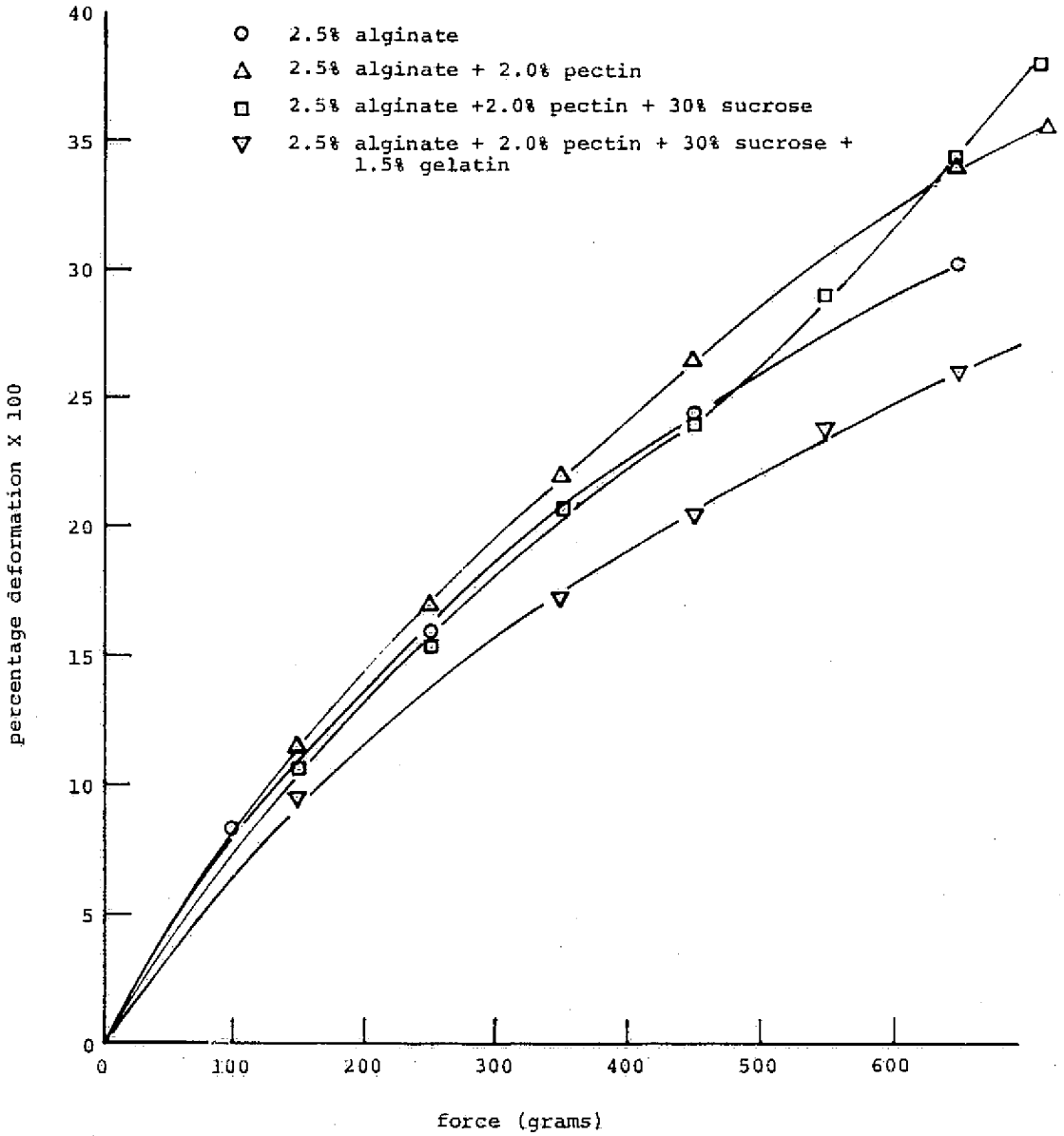
Figure 10 Stress-strain curve of cucumber under compression loading (crosshead speed 5 cm/min.)

Figure 11 Stress-strain curve of apple (Red Delicious) under compression loading (crosshead speed 5 cm/min.)

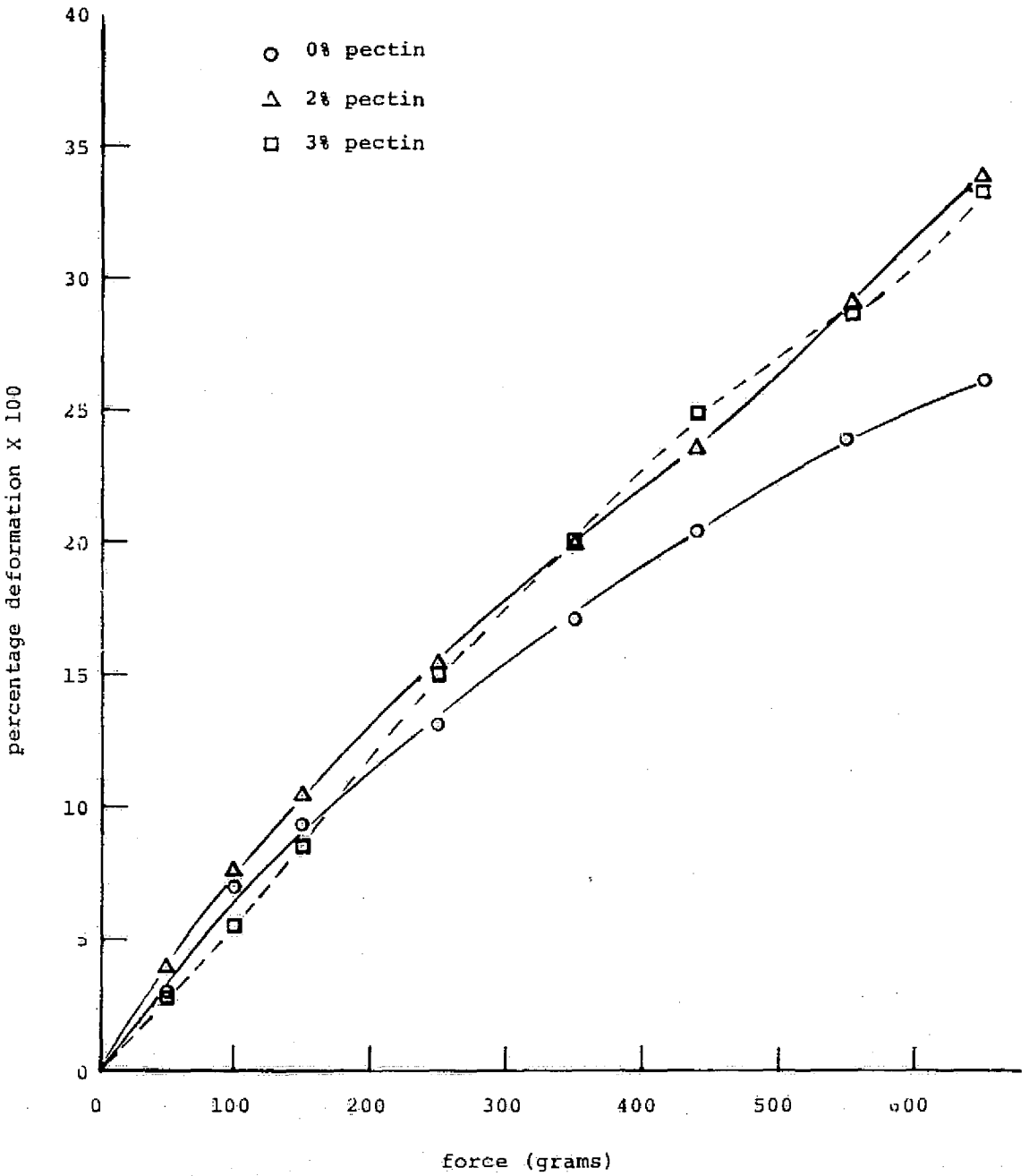
Figure 12 Stress-strain curve of pear (Bartlett) under compression loading (crosshead speed 5 cm/min.)



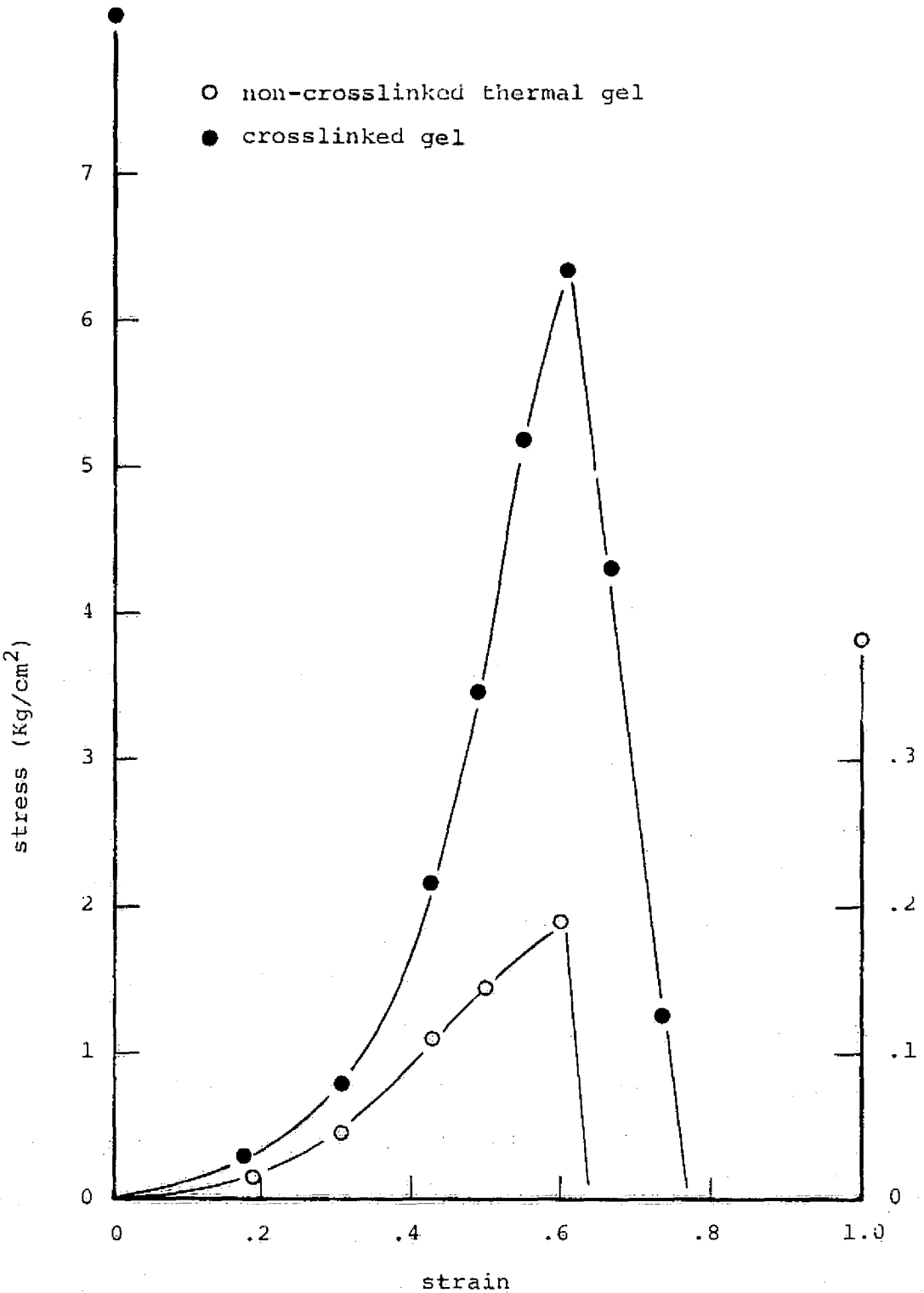
Effect of crosslinking and alginate concentration on the load-deformation behavior of gels containing 30% sucrose, 2.0% pectin and 1.5% gelatin.



Effect of pectin, sucrose and gelatin on the load-deformation behavior of 2.5% alginate gels.



Effect of pectin concentration on the load-deformation behavior of 2.5% alginate gels containing 30% sucrose and 1.5% gelatin



Comparison of stress-strain curve of crosslinked alginate gel and thermal set gelatin gel of the same composition (2.5% alginate and 1.5% gelatin) (crosshead speed 20 cm/min.)

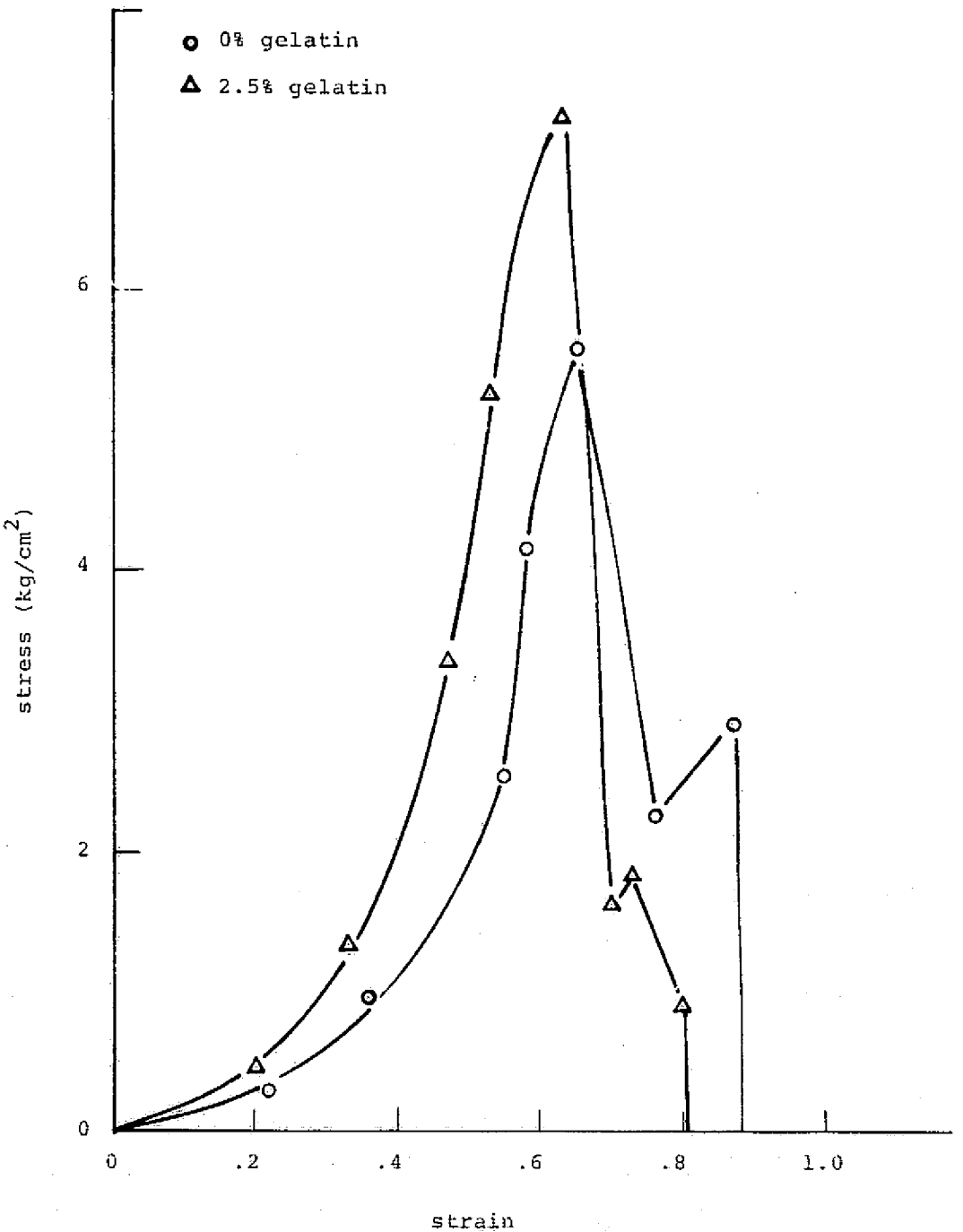
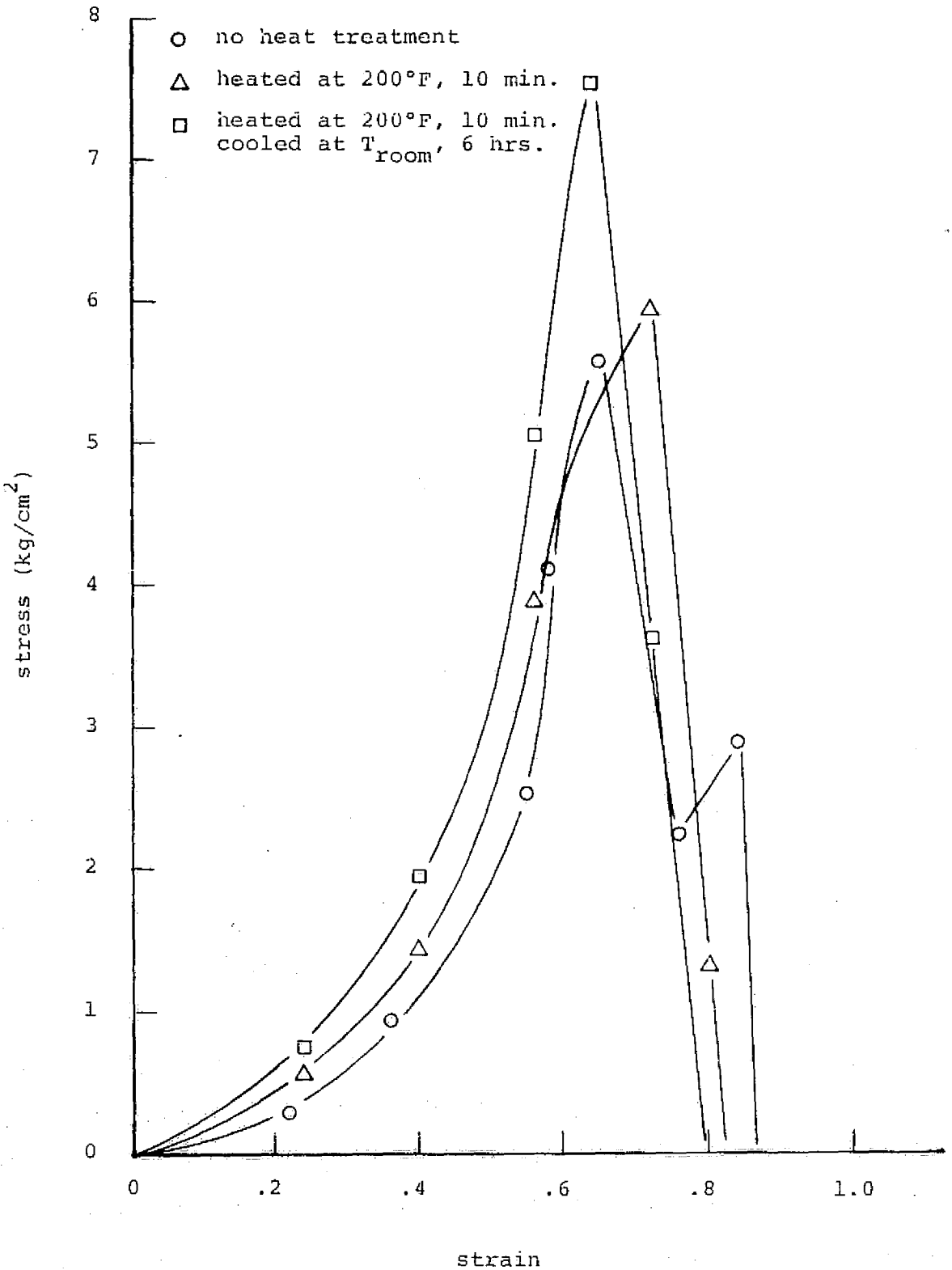
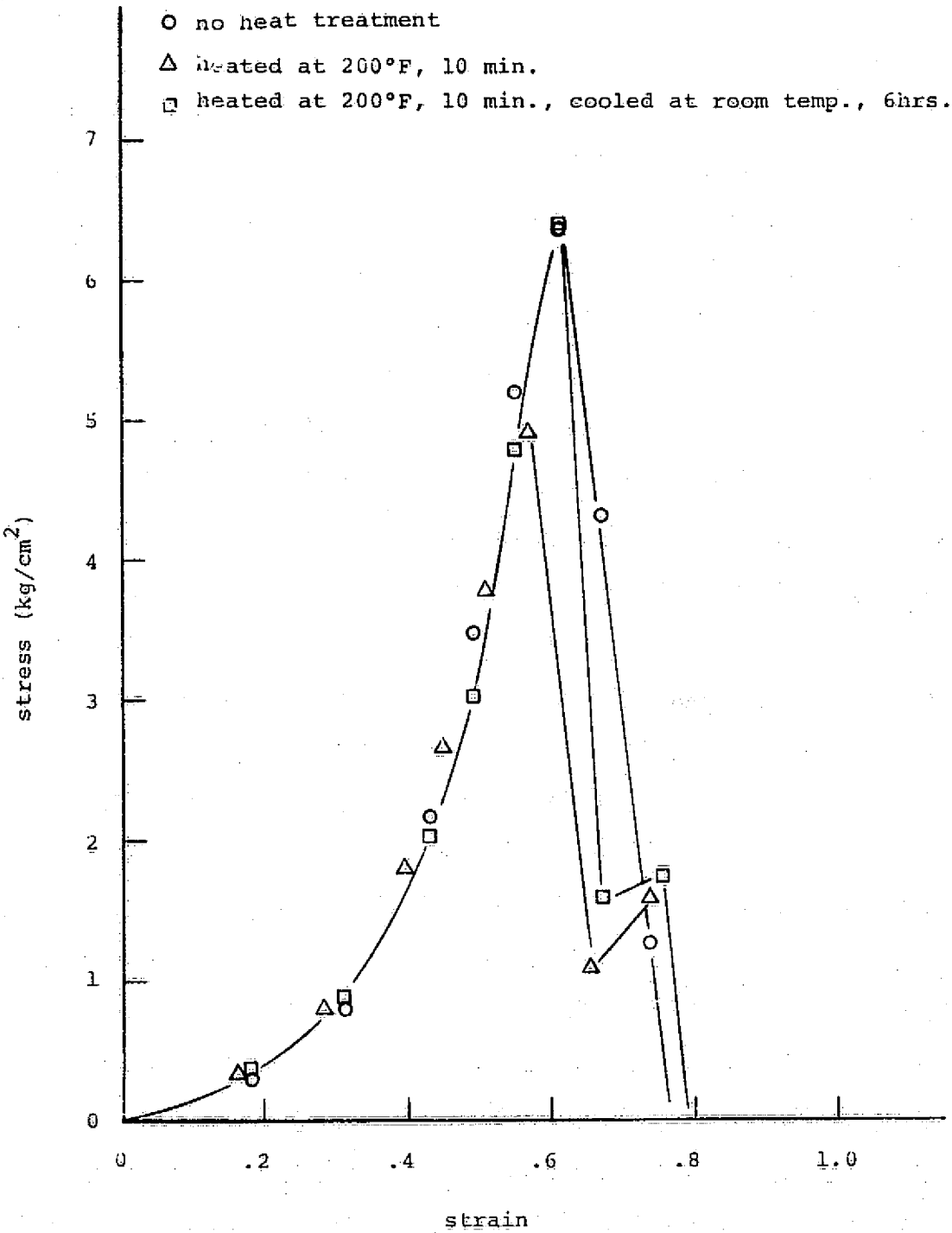


Figure 8. Effect of gelatin on the stress-strain behavior of 2.5% crosslinked alginate gels (crosshead speed 20 cm/min.)

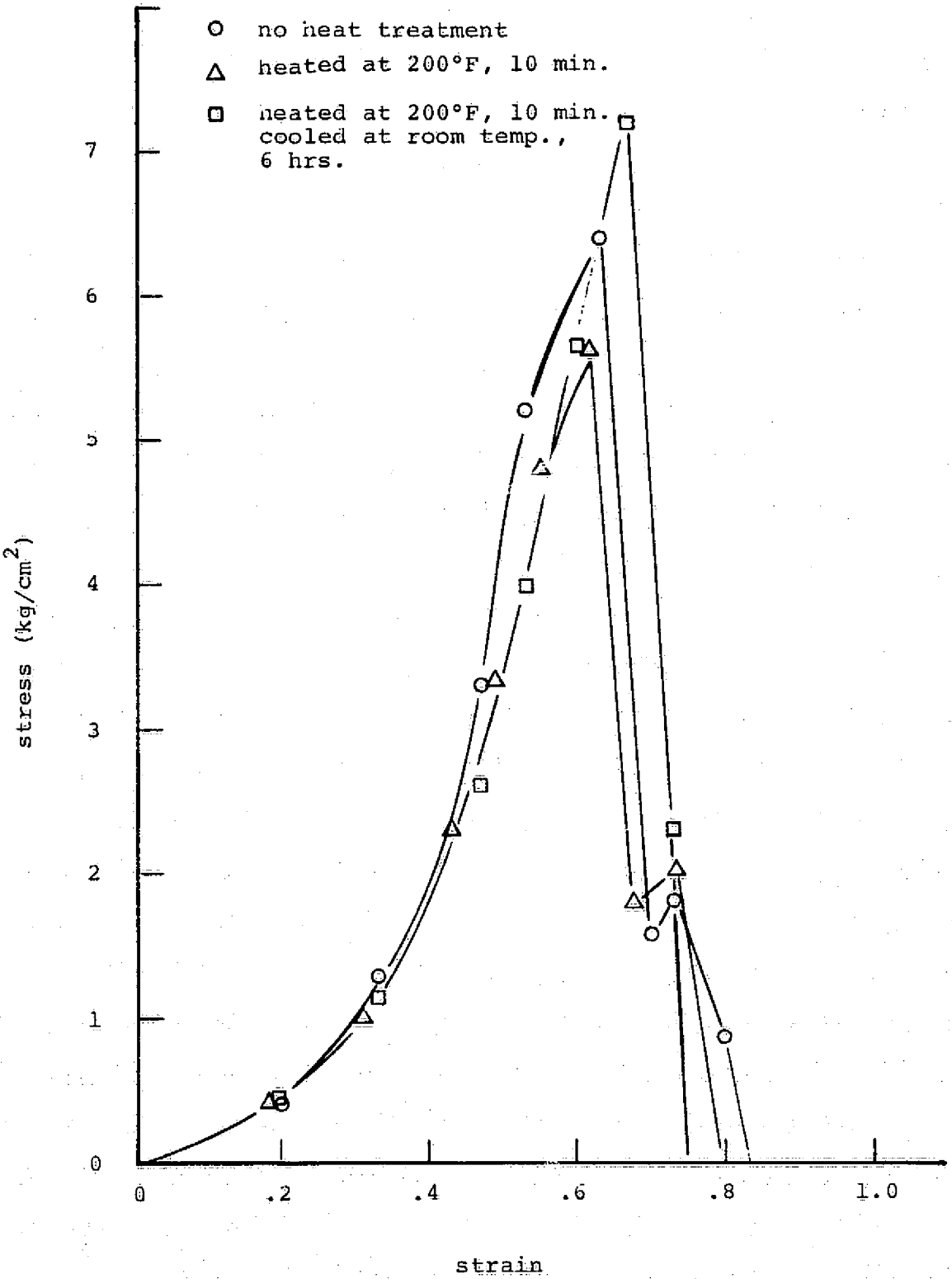


Effect of heat treatments on the stress-strain curve of pure 2.5% alginate gels. (crosshead speed 20 cm/min.)

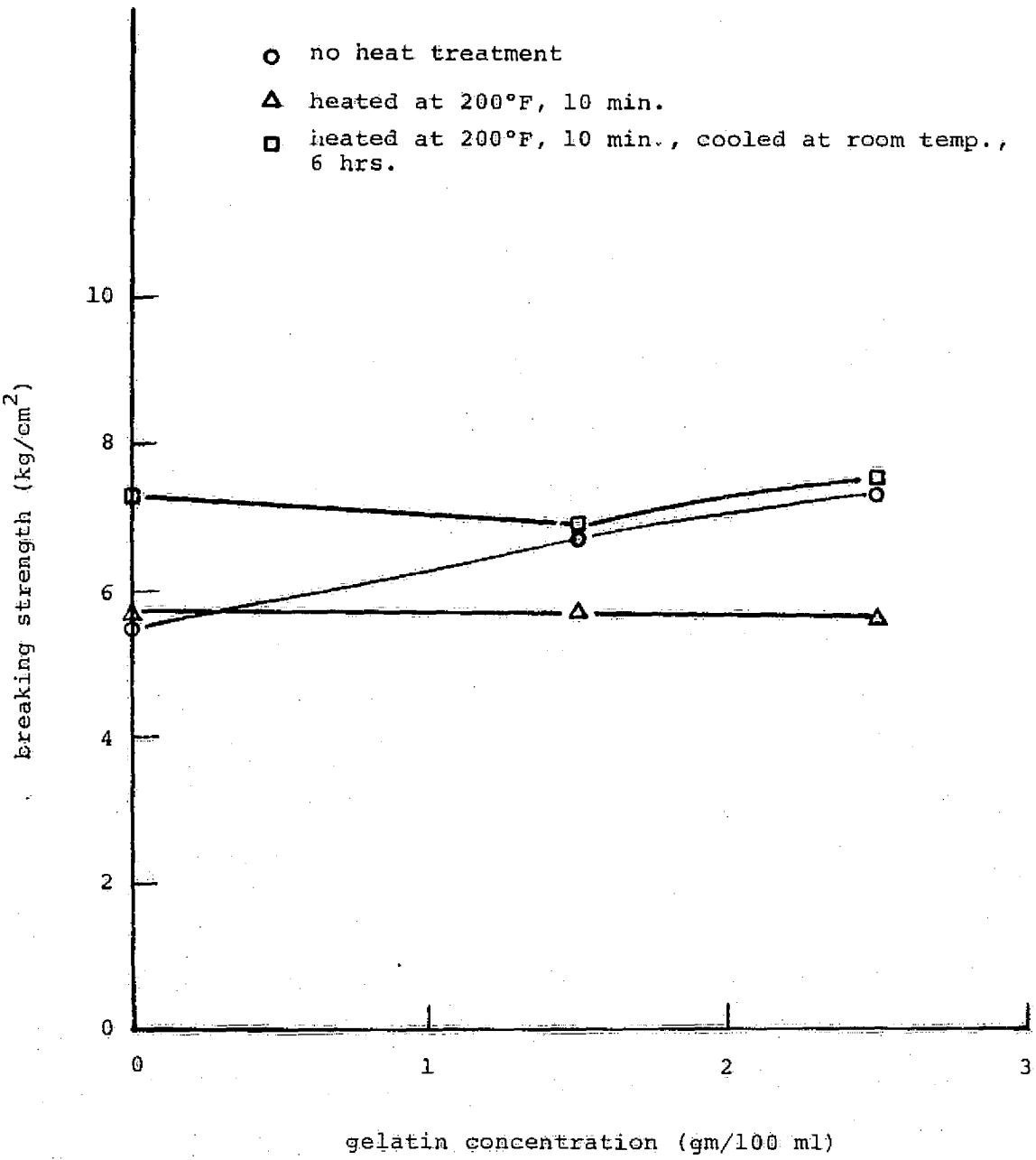


Effect of heat treatments on the stress-strain curve of 2.5% alginate gels containing 1.5% gelatin (crosshead speed 20 cm/min.)

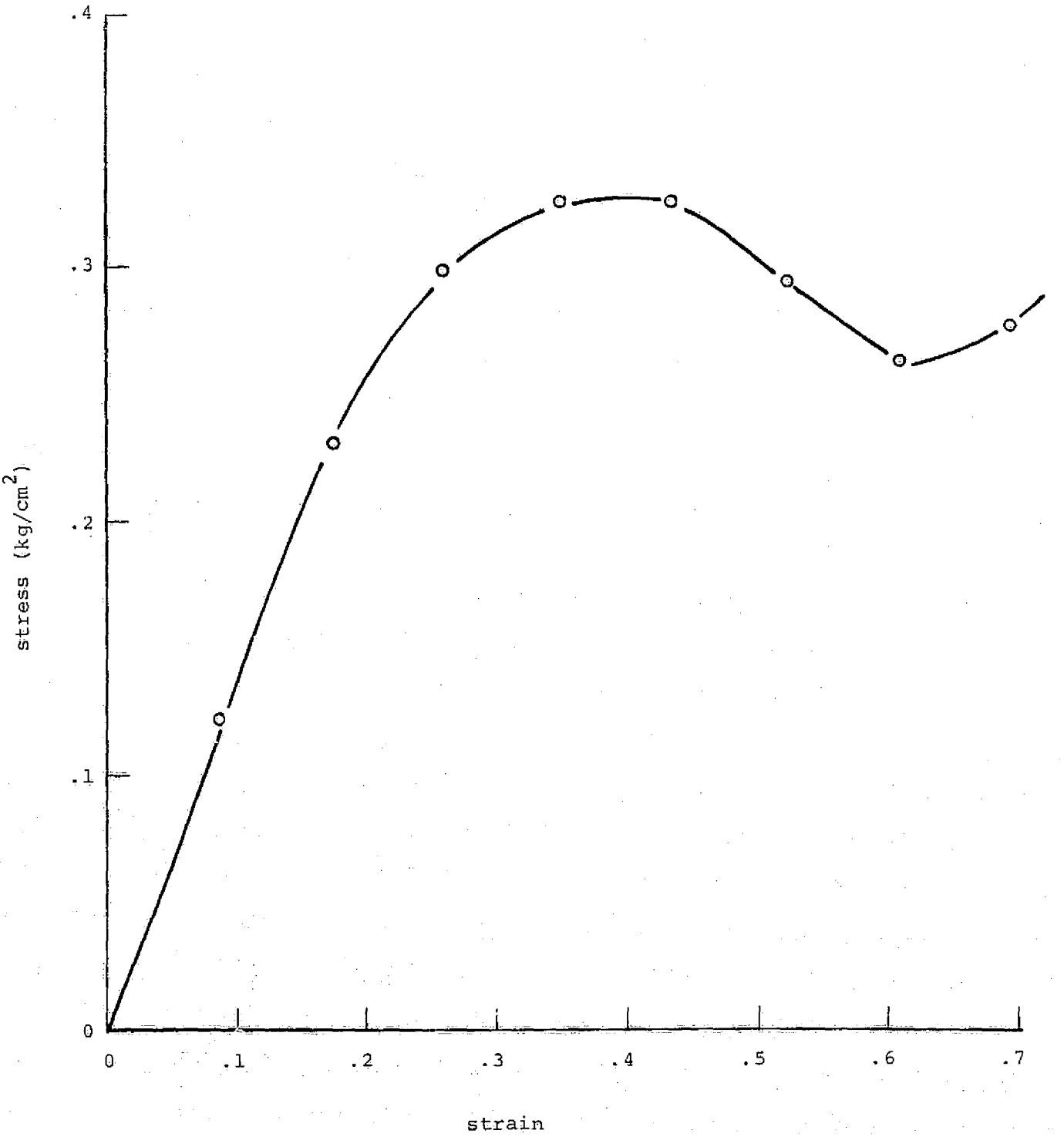
C.2



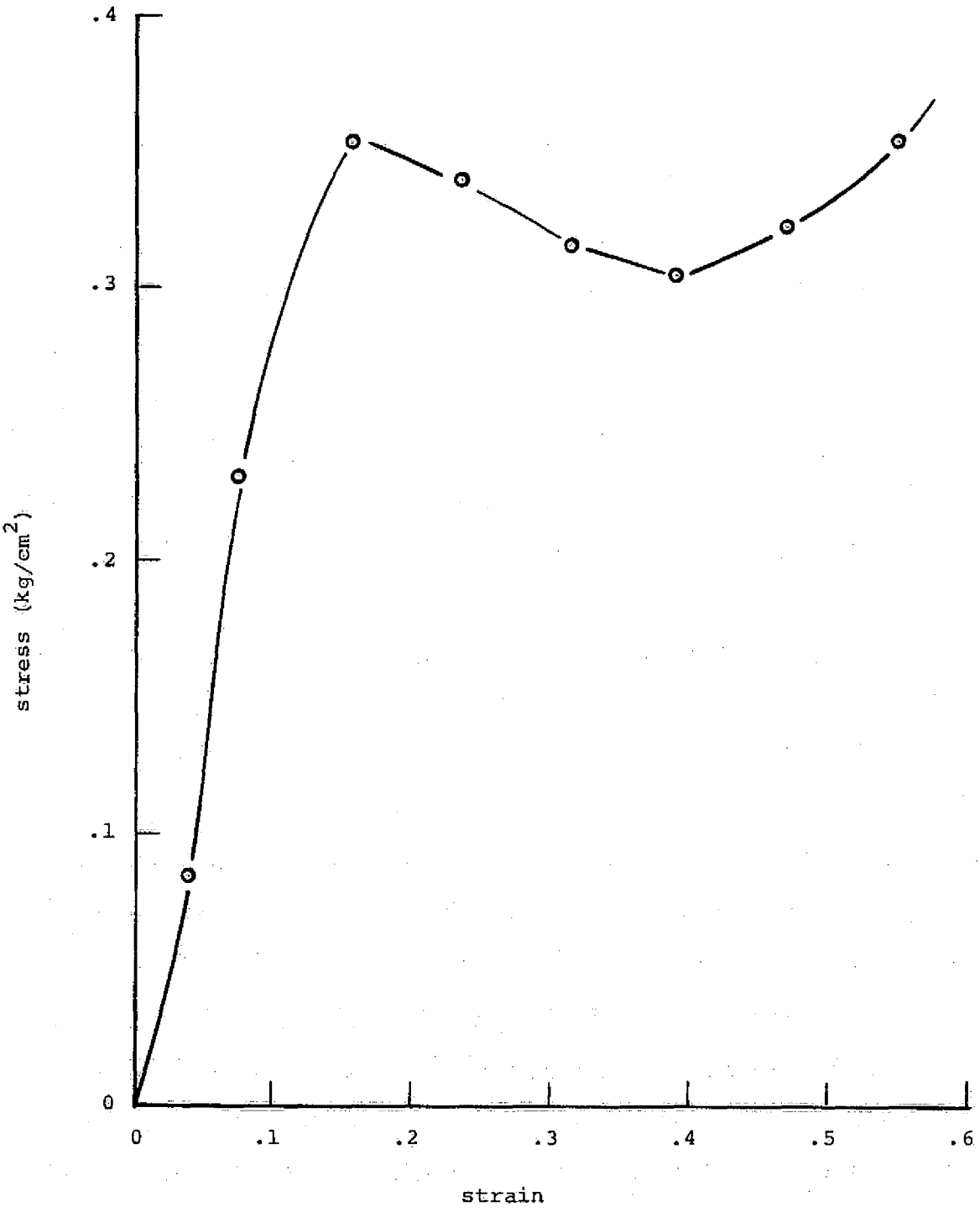
Effect of heat treatments on the stress-strain curve of 2.5% alginate gels containing 2.5% gelatin (crosshead speed 20 cm/min.)



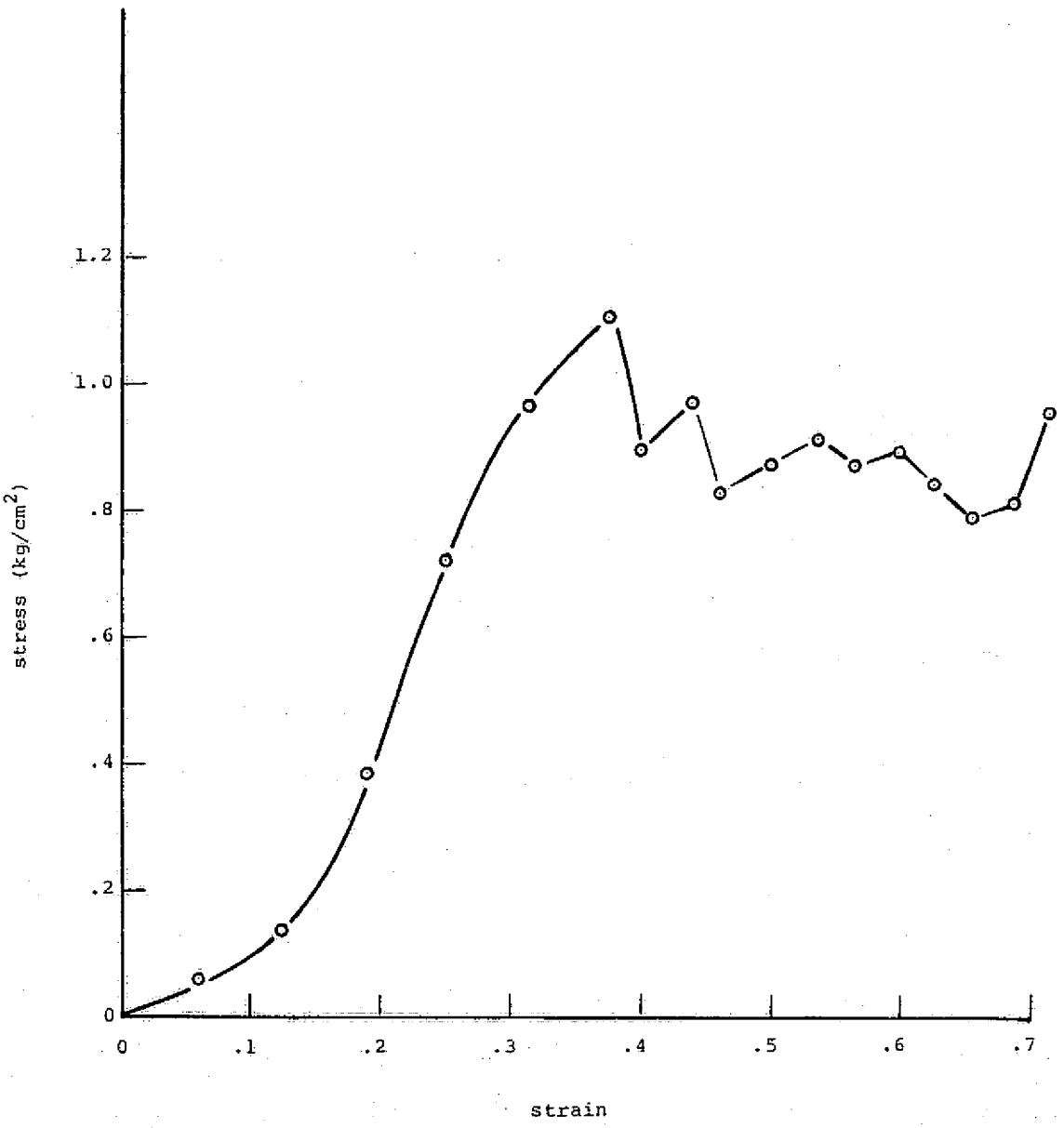
Effect of heat treatment on the breaking strengths of 2.5% alginate gels containing different gelatin concentrations



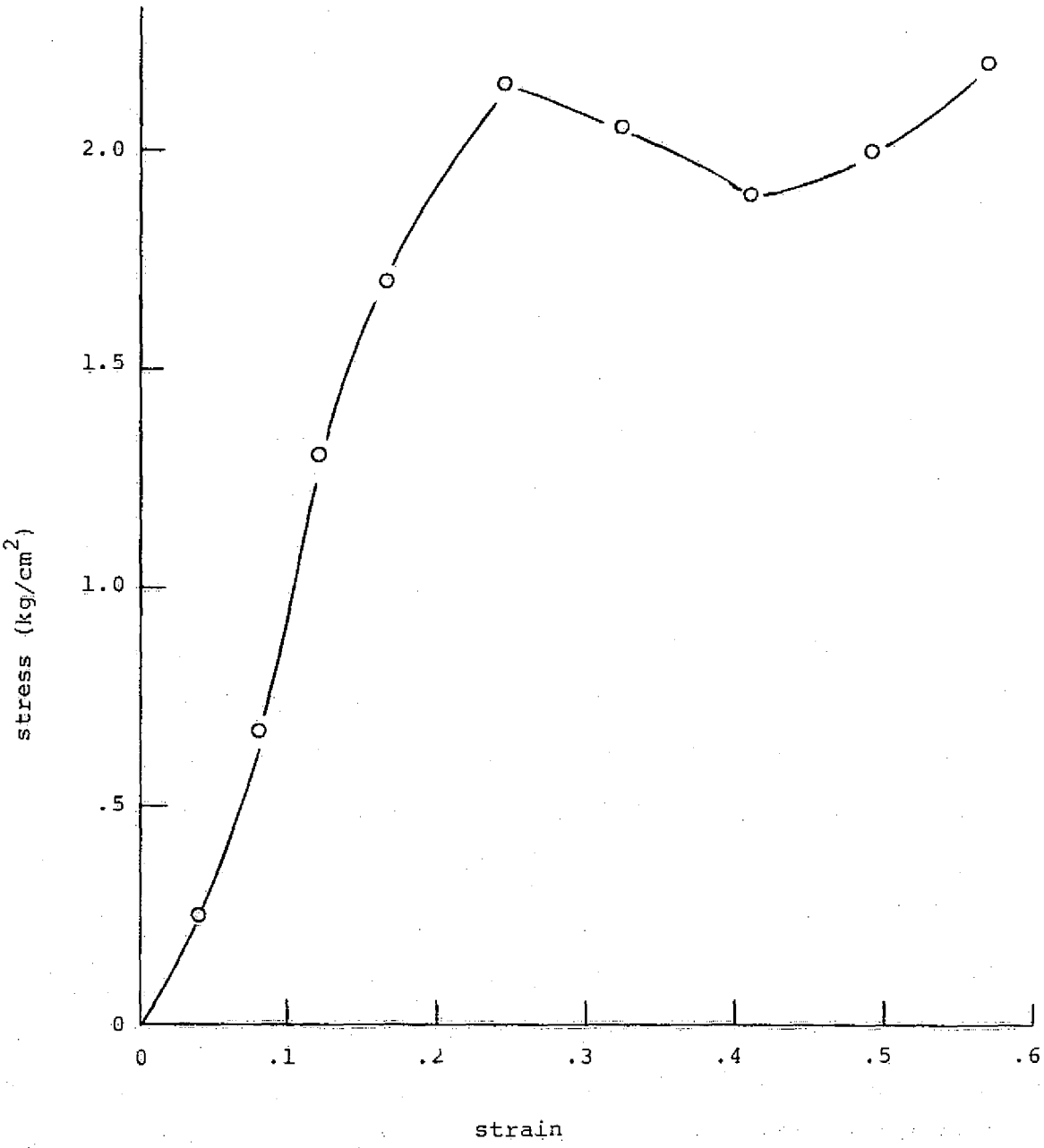
Stress-strain curve of banana under compression loading (crosshead speed 5 cm/min.)



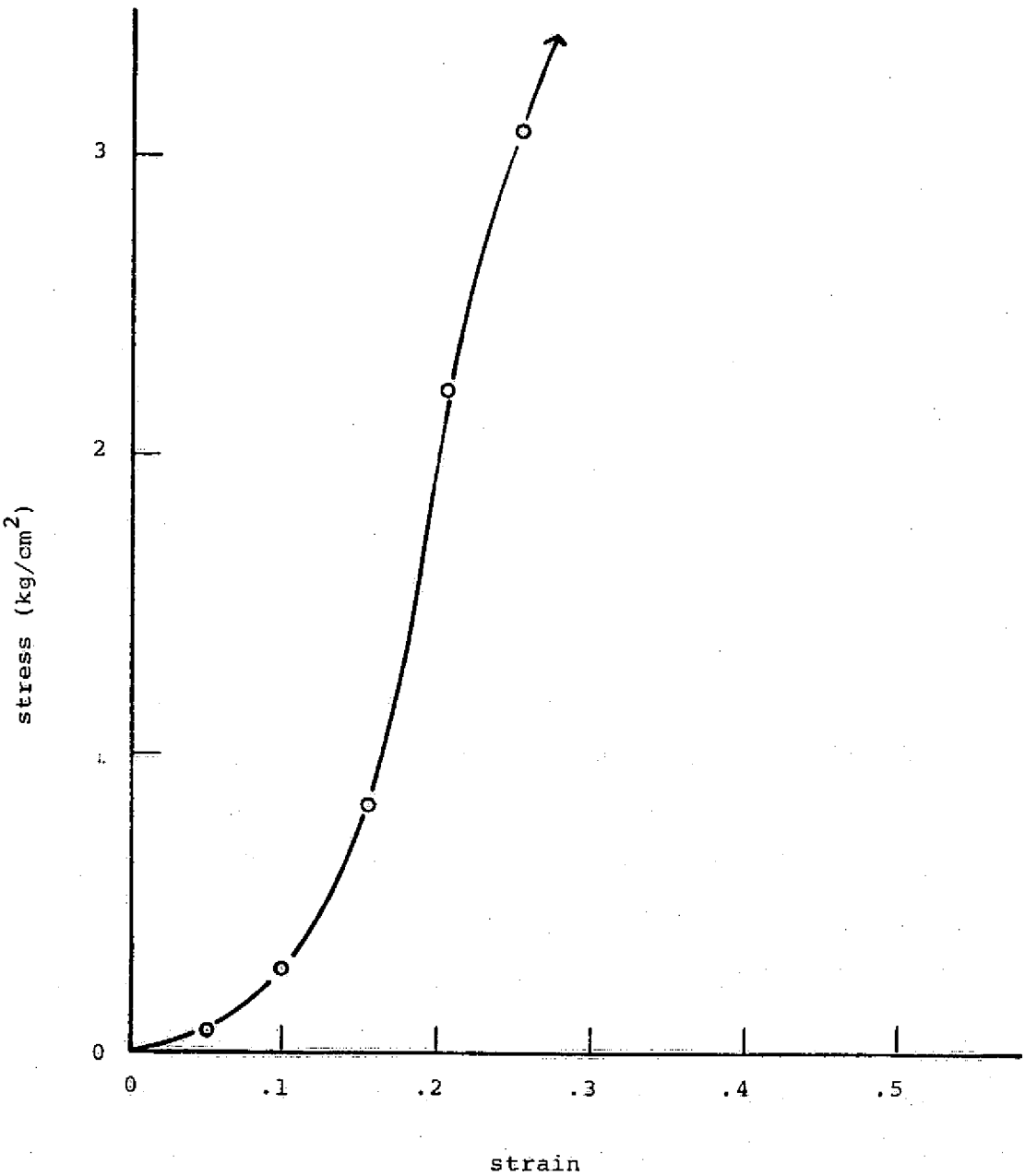
Stress-strain curve of peach under compression loading (crosshead speed 5 cm/min.)



Stress-strain curve of cucumber under compression loading
(crosshead speed 5 cm/min.)



Stress-strain curve of apple (Red Delicious) under compression loading (crosshead speed 5cm/min.)



Stress-strain curve of pear (Bartlett) under compression loading (crosshead speed 5 cm/min.)

Appendix to Section 4

Two-step Gelling Procedure for Preparing Artificial Food Matrices

The two-step gelling procedure for preparation of the Artificial Food Matrices (AFM) is outlined in the accompanying flow chart (Figure A-1). The source of ingredients are given in Table A-1. A detailed description of the process is given below for the preparation and processing of a batch which would yield approximately 110 grams of AFM prior to osmosis. This will yield approxmately 21 grams of freeze dried AFM.

Step 1: High-methoxy pectin (2.0g), sodium alginate (2.5g) and Avicel (0.25g) were manually dry mixed using a spatula.

Step 2: Sucrose (30g) was dissolved in 100 ml of water and the solution heated to approximately 90°C. Unflavored gelatin powder (1.5g) was added to the hot solution and mixing on a stirring hotplate continued till the the gelatin dissolved completely. The hot gelatin-sucrose solution was added to a Waring blender and the dry mixed powder (from Step 1) added. The blender was then run about 1 minute so that all the powder was dispersed. If some powder adhered to the blender cup wall, a spatula was used to return it to the liquid and the sample was mixed again.

Step 3: The homogenized solution was transferred to a container and placed in a refrigerator at approximately 4°C to allow the gelatin gel to set.

Step 4: The thermally gelled sample was hand sliced into uniform pieces of the desired size and shape.

Step 5: The cut thermal gelled pieces were place in an unagitated 4.5% calcium lactate solution at room temperature to give the cross-linked calcium alginate gel. The time for crosslinking is dependent on the piece dimensions. Values of crosslinking times as a function of piece minimum dimension are given in "Luh et al, J. Fd. Sci. 41:89 (1976)" (Section 4.2 of the Phase IV Annual Report.

Step 6: The cross-linked samples were rinsed with running water to remove adhering calcium lactate solution. The pieces were then placed in a gently agitated 60% sucrose solution at room temperature for 4 hours to remove about 20-30% of the sample water.

Step 7: Following osmosis, the samples were rinsed quickly with running water to remove adhering sucrose solution. At this time the flavoring agent could be added if it is desired that the freeze dried pieces have a particular

character. (This was done only for the case of pieces to be used for simultaneous freeze drying with yoghurt.) The pieces on a tray were covered with aluminum foil and frozen in a cold room at -30°C for at least 12 hours (overnight).

Step 8: The covering aluminum foil was removed from the frozen samples and the trays placed on the freeze dryer shelves which had been pre-cooled to -20°C. The chamber was evacuated at 0.1 Torr for 12 hours before the shelf cooling was terminated. The drying then proceeded for 2 days without external applied heating.

Step 9: The chamber vacuum was broken with dry air and the samples stored in various containers including glass jars, tin cans, etc.

Step 10: Rehydration was conducted by immersing or mixing the dry sample or pieces in cold water. The time for rehydration depended on piece size, with cubes approximately 0.5 cm on an edge requiring about 5 minutes. The amount of water per unit weight of product depended on if the AFM was incorporated in a product or was alone. For example, AFM alone could be rehydrated in an excess of water and then drained. A product such as yoghurt with AFM required a precise addition of water to insure proper

consistency (3 parts of water by weight per 1 part of dried yoghurt with AFM). If desired, unflavored freeze dried AFM pieces can be rehydrated with water containing desired flavoring ingredients to give the flavored AFM for incorporation into the final product.

Table A-1 : Ingredients for AFM

AFM Ingredients[a]

Pectin, High-methoxy	Citrus P-9135	Sigma Chem. Co.
Sucrose	Commercial	
Avicel	PH-101	FMC Corp.
Sodium Alginate	Kelco Gel LV (KGLV 2475-52)	Kelco Co.
Gelatin, unflavored	Commercial	Knox Co.
Flavoring Components used:		
Imitation Pineapple flavor (F-4963)		Givaudan Corp.
Imitation Cherry flavor (F-1311)		Givaudan Corp.
Imitation Peach flavor (F-4710)		Givaudan Corp.
Imitation Pear flavor (F-6599)		Givaudan Corp.
Imitation Strawberry flavor (-)		Givaudan Corp.

Crosslinking agent

Calcium Lactate	N.F. Powder	Mallinckrodt Chem. Works

a) Concentrations used are given in text. Flavorings generally adjusted by trial. For large scale pineapple yoghurt preparation 0.45 ml of F-4963 was used per 8 oz. (225g) of yoghurt.

Number	Step
1	Dry mixing of pectin, alginate and Avicel
	↓
2	Homogenization of dry mixture with hot sucrose-gelatin solution
	↓
3	Refrigeration to form thermal-set gelatin gel
	↓
4	Slicing of thermal-set gelatin gel
	↓
5	Crosslinking of alginate in calcium lactate solution
	↓
6	Osmotic Concentration of AFM
	↓
7	Freezing
	↓
8	Freeze Drying
	↓
9	Storage
	↓
10	Rehydration

Figure A-1

Two-Step Gelling Procedure for Preparing Artificial Food Matrices

5. Osmotic Preconcentration to Yield Improved Quality Freeze Dried Fruits

5.1 Introduction

In Phases I, II and III of this contract, fundamental studies into factors affecting the retention of desirable organoleptic qualities of freeze dried liquid based model systems led to the development of a set of processing criteria which should result in freeze dried food products of improved organoleptic quality. The process criteria for improved product quality were increase of initial solids content to 25% or above, and utilization of slow freezing (freezing times of about 1 hour). During Phases I-III, technologies were developed to utilize these process criteria for the production of freeze dried fruit slices. A series of organoleptic tests were conducted with a wide variety of fruit products in order to evaluate if significant product improvement were attained using the new technologies developed in this contract. Results presented in the Phase II and III Annual Reports demonstrate that the fruit products prepared according to the technologies developed in this contract have been rated superior to conventionally freeze dried fruit products. An extremely high level of acceptibility by the lay public has been noted on occasions when product has informally been served to groups of such people.

The process criteria of increased solids content prior to freeze drying is easily accomplished in the case of liquid foods, where evaporation of solvent or addition of solutes can be undertaken.

With solid food pieces, the increase in solids content is much more difficult to achieve. The use of osmotic pressure differentials and solute diffusive flow to give selective removal of water and uptake of solutes by solid food pieces has been investigated in this contract. As noted above, this preconcentration technique has resulted in freeze dried fruit products of improved quality.

In Phase II and III of this contract, the osmotic preconcentration technique has, in large part, utilized sucrose solutions at 60% solids as the osmosis medium. During Phase III, maltodextrin of DE=15 was included in some tests to investigate the possible effect that sucrose sweetness might have on evaluation of product quality. It was noted that while highly acceptable products were obtained with either sucrose or maltodextrin, in all cases there was a preference for the fruit slices with the sucrose osmosis treatment. It was noted in the Phase III Annual Report that this could be the result of a number of factors, operating singly or in combination. These factors include:

a) increased sweetness of sucrose treated product

b) higher solids content achieved with sucrose treatment

c) inherent ability of sucrose to better retain organoleptic quality properties

In Phase IV, the study of osmotic preconcentration of freeze dried fruits has been expanded to include evaluation of a number of process parameters and investigation of additional materials as osmotic solutes.

Of special interest has been mixed solute systems. Knowledge

of the effect of process parameters on the kinetics of preconcentration can be used to prepare fruit samples of similar solids content from different solute materials. Knowledge of preconcentration kinetics is also necessary for improvements of process design. Evaluation of new solutes for their effectiveness in osmotic preconcentration is necessary so that solutes of reduced sweetness can be identified. Sucrose, which has a high level of sweetness, has proven very acceptable for osmotic preconcentration of fruit slices, products which normally have an above average sweetness level. Application of the osmotic preconcentration process to food solids of lower normal levels of sweetness requires the development of less sweet osmotic solutes. Additionally, solutes of lower sweetness, when used in conjunction with fruits may yield high quality products of organoleptic characteristics which differ from those produced with sucrose. Additionally sucrose is a rather costly solute relative to other available materials of potential usefulness. The economic considerations will be particularly important in technology transfer from space applications to the civilian economy.

5.2 Summary of Studies On Organoleptic Quality of Osmotically Preconcentrated Freeze Dried Fruits

In the past year, three articles were prepared which document studies on improved techniques for fruit products conducted under this contract. One has recently appeared in the Journal of Agriculture and Food Chemistry. A reprint of this article is included in this report. The other papers are "in press" in the "Proceedings of the IV International Congress of Food Science and Technology". The page proofs of these papers are included with this report.

Journal of Agricultural and Food Chemistry

© Copyright 1975 by the American Chemical Society

Volume 23, Number 6 November/December 1975

ORIGINAL PAGE IS OF POOR QUALITY

SYMPOSIUM ON FLAVOR CHEMISTRY OF PROCESSED FOODS

The following papers were among those presented in the Symposium on Flavor Chemistry of Processed Foods, 168th National Meeting of the American Chemical Society, Atlantic City, N.J., Sept 1974.

Process Conditions for Improved Flavor Quality of Freeze Dried Foods

James M. Flink

Studies on the retention of flavor during freeze drying, conducted primarily with model systems, have led to the development of mechanisms by which flavor retention phenomena may be explained, and to specification of process conditions to optimize flavor retention. Of greater value is their ability to predict processing conditions giving improved flavor quality for real food materials. Process parameters of greater significance are freezing rate, initial solids content, and conditions which result in maintenance of sample structure. The present paper reviews results of studies in which the flavor retention behavior of real food products, both liquid and solid, has been evaluated. These include coffee, fruit and vegetable juices, and fruits. In most cases, flavor quality for the real food showed the same behavior relative to process conditions as predicted by the mechanisms based on model system studies.

Freeze drying is generally considered to be the dehydration process which will result in the highest quality dehydrated products. This is due to the fact that water is removed without the presence of a free liquid phase, and that heated regions in the dry layer have low moisture contents, while regions of high moisture have low temperatures. One of the crucial quality aspects, maintenance of product flavor, has aroused much interest in the recent past, as it was felt that flavor components, many of which are highly volatile, would be largely lost during the process since the freeze drying is generally conducted at absolute pressures of below 1 Torr.

Most early studies on the retention of flavor during freeze drying have concentrated on simple model systems in which complications due to compositional variations of natural products could be avoided. By means of these studies, in which simple quantitative retention information could be easily evaluated and correlated with changes in process variables, two mechanistic interpretations of flavor retention phenomena during freeze drying were proposed. These were labeled the "selective diffusion" mechanisms (Menting and Hoogstad, 1967; Thijssen and Rulkens, 1968; King and Chandrasekaran, 1973) and the "microregion entrapment" mechanism (Flink and Karel, 1970a) by their respective proponents. These mechanisms have been reviewed recently by King (1971), Thijssen (1973), and Flink (1973). It appears that there is some agreement that these two proposed mechanisms probably are describing the same basic phenomena from two different approaches, namely mathematical or macroscopic vs. morphological or microscopic viewpoints.

Before presenting some of the results obtained with model systems, it might prove valuable to make the fol-

Department of Nutrition and Food Science, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.

Table I. Retention of 1-Propanol by PVP[a] following Freeze Drying

Initial volatile concn, ppm	Volatile retention, %	Volatile retained, ppm
50	67	33
100	59	59
800	28	224
10,000	26	2600
20,000	25	5000

[a] Initial PVP concentration = 20%.

lowing observations regarding the use of model systems, since to some this may not seem to be a valid approach to determining what will occur in real foods. It has been noted above that natural foods are subject to compositional variations which lead to an undesirable complication regarding analysis of experimental data. Furthermore, the number of components which would require monitoring, just to be sure which are varying, would greatly increase the experimental burden. Thus, model systems were envisioned as serving as simplified versions of real foods, in which compositions were predetermined and thus well known. The concentrations of all components were independently variable.

In the present era of food processing, model systems may be considered to serve dual roles since besides modeling real foods they are simplified formulated foods. More and more, foods are being produced by mixing a number of individual ingredients together and processing the mixture. This is precisely the method for producing a model system.

It has sometimes been noted that the concentrations of the model flavor compounds present in the model systems are much higher than concentrations generally shown to be present in real foods, a situation arising from considerations of analytical procedures for the large numbers of samples to be evaluated. While it would seem that data at lower volatile component concentrations would be extremely valuable, the information obtained at the higher concentrations is directly applicable to the freeze drying of preconcentrated feeds, or use of freeze drying to prepare encapsulated flavor concentrates.

In the course of developing mechanisms to explain flavor retention phenomena, a sizable body of data has been obtained on the influence of process conditions on retention of model flavor compounds in model systems. Only a small fraction of this information can be presented here; more information is available in the articles listed under Literature Cited.

PROCESS CONDITIONS AND FLAVOR RETENTION IN MODEL SYSTEMS

A number of processing variables have been investigated, and while the listing below may seem exhaustive, it is likely that there exist others which were unfortunately omitted from this listing. Under each processing variable will be given one or more references from which the information was obtained. It should be emphasized that other references listed under Literature Cited will contain information on one or more of the processing variables.

(1) **Solids Composition.** The influence of the type of solid component on volatile retention has been demonstrated in almost all model system studies published, though direct comparison between studies is hazardous due to the variation of other process parameters. Flink and Karel (1970b) presented a tabulation of the retention of various volatile compounds by a variety of mono-, di-, and polysaccharides freeze dried under "identical" conditions. In this case, for most volatiles studied the disaccharides were the most effective, the monosaccharide next, followed by the polymer. In other studies (Chirife and Karel, 1974a) proteins were shown to be effective solids for retention of volatile components.

Studies on binary solid systems at a fixed total solids concentration have shown variable results (Ofcarcik and Burns, 1974; Flink, 1970). For some mixtures retention has improved in a synergistic manner, while in others no effects are noted. It seems likely that this variable behavior is related to the influence of the substituted species on the resultant structural stability of the freeze drying matrix ("collapse"). Thijssen (1972b) has shown how the retention of propanol decreases as glucose is substituted for maltodextrin when freeze drying at an ice front temperature of −25°.

Synergistic effects may result from changes in matrix properties if freezing results in different phase structures of the matrix. Gejl-Hansen (1971) observed freeze dried mixed maltose–maltodextrin systems microscopically. At intermediate levels of maltose substitution, the "dendritic" matrix structure changed to a "cubic cellular" appearance, though eventually, at higher levels of maltose substitution, the dendritic structure reappeared. Unfortunately, volatile retention behavior was not evaluated.

(2) **Solids' Concentrations.** Manipulation of the solids' concentration can be evaluated in two manners, the percentage retention of the initial volatile or as the retention of volatile per unit weight of solid. These two methods, which are of value for different purposes, will give different interpretations. In the discussion which follows, the percentage retention of initial volatile will be used, since that value is most reported in the literature.

Many researchers have noted the importance of the initial solids' concentration on the retention of volatile compounds during freeze drying. Chirife et al. (1973) and Thijssen (1973) have presented information showing that, at low solids' concentrations (below 10–20%), increases in solids' concentration greatly increases volatile retention. When the initial solids' concentration is greater than about 25%, there is little effect of further increases on volatile retention. The initial solids' concentration at which volatile retention attains its asymptotic value appears to depend on the volatile species and solid species present in the model system.

If the above observations are considered on a unit weight of solids basis, it is seen that there exists an optimum solids' concentration at which the volatile retained per unit of solids is a maximum. This optimum will be lower than the solids' concentration at which the volatile retention reaches its asymptote.

(3) **Initial Volatile Concentration.** Similar considerations as noted above relative to the method of evaluation must be made. While it has become customary to present volatile retention as a percentage of the initial volatile content, it should be recognized that, for a fixed solids concentration, it is possible that as the initial volatile concentration increases, the percentage volatile retention can decrease while the absolute amount of volatile retained is increasing (and thus the volatile per unit of solids is also increasing). This is shown in Table I using the data of Chirife et al. (1973). Based on this evaluation, it is difficult to say if the volatile retention has decreased or increased.

Over the range of concentrations most often studied (initial volatile concentration below 1%), it appears that the percentage retention is relatively constant until low concentrations (100–1000 ppm) are reached, at which point the retention increases.

It should be noted that an opposite effect is reported by Voilley et al. (1973) in that increases of initial volatile concentration result in increases in percentage retention.

(4) **Freezing Rate.** The rate of freezing will influence the structure of the freeze dried material as it controls the size of the ice crystals and the degree of solute concentra-

Table II. Retention of Flavor Components of Apple Juice following Partial Freeze Drying

	Flavor retention, %, at solids' content of			
	17%[a]	26%	36%	44%
Ethyl acetate region	78	74	75	80
n-Hexanal region	61	60	73	70
2-Hexenal region	66	65	80	78
n-Hexyl acetate region	50	50	70	70

[a] Only 10% of initial water removed.

tion achieved in the matrix phase. The rate of freezing is one of the most investigated process variables and it can be noted that in all cases reported, slow freezing results in improved retention of the volatile components. The improvements in volatile retention which depend on the retention levels have been reported for the most part to be 2 to 3 times (i.e., if rapid freezing gives 20% retention, slow freezing would give 40–60% retention) (Chirife and Karel, 1974a,b).

(5) **Drying Rate.** The rate of freeze drying can be varied in a number of ways, for example by increasing the ice front temperature to improve mass transfer or by increasing the heating plate temperature to improve heat transfer. These changes can be expected to influence volatile retention by means other than just drying rate. In any case, Thijssen (1972a) calculated the effect of drying rates on volatile retention and showed that higher retentions resulted with rapid drying. This was experimentally demonstrated by Rulkens and Thijssen (1972) by maintaining the ice front temperature constant while heating through the frozen layer and controlling the rate of drying by manipulation of the chamber pressure. As an example, drying at chamber pressures giving a doubling of the drying rate at an ice front temperature of −20° resulted in an increase in 1-propanol retention from 65% (slow drying) to 80% (rapid drying). The observed results are sensitive to volatile species and ice front temperature.

(6) **Sample Dimensions.** The influence of the sample dimensions has been reported for slabs (Chirife et al., 1973) and for layers of granules (Thijssen, 1972b). Sample dimensions which result in improvements in drying rate (thinner slabs or thinner layers of granules) generally will give increased retention of the volatile.

The relationship of diameter of the individual granule to volatile retention is more complex, as there exists for any layer thickness a granule size at which volatile retention is optimum, even though drying rates decrease as the granule size increase (Rulkens and Thijssen, 1972). Since the optimal granule size increases as the freezing rate decreases, it appears that for small particles there is a relationship of total granule dimension and ice crystal dimension which is important relative to volatile retention.

(7) **Frozen Layer Temperature and Collapse.** The influence of frozen layer temperature has already been alluded to above. Thijssen (1972a) and Voilley et al. (1973) have shown that as the ice front temperature increases, the retention of volatile compounds decreases. Increases in ice front temperature which do not result in collapse of the drying matrix will nevertheless result, according to the phase diagram, in a decrease of the matrix solids' concentration due to the melting of some of the ice crystals.

Collapse is a phenomenon in which the matrix undergoes structural degradation due to the onset of viscous flow. Collapse of the freeze drying matrix results in substantial loss of the volatile components, with the loss being directly related to the extent of collapse (Bellows and King, 1973).

ORIGINAL PAGE IS OF POOR QUALITY

Table III. Relative Retention of Coffee Volatiles (Based on Total Peak Area) for Various Freezing and Freeze-Drying Conditions

Freezing conditions[a]	Rel retention, %,[b] at freeze-drying chamber pressure, Torr						
	0.2	0.3	0.4	0.5	0.6	0.7	0.8
Very slow	92	96	78	77	66	67	34
Slow	100	99	88	82	91	82	35
Foam, slow	67	61	49	53	57	44	63
Quick	47	53	38	38	44	35	36
Foam, quick	48		42	42	43	32	29

[a] Very slow, stepwise to −40°; slow, −40°; quick, spray onto chilled drum at −52°. [b] Relative to slow frozen sample dried at 0.2 Torr, from Ettrup-Petersen et al. (1973).

Table IV. Flavor Loss Tolerances for Heating Coffee Granules during Freeze Drying

Temp, °C	Time at given temp, hr	
	No noticeable flavor loss	No significant flavor loss
40	3.75	7.5
60	2.25	4.5
80	1.5	2.5

(8) **Heat Input Conditions.** Heat input to the sample will influence a number of factors, such as drying rate, temperature gradients, ice front temperature, etc. It has already been shown that drying rate will influence the retention of volatile compounds. Rulkens and Thijssen (1972) have shown that, if the ice front temperature is maintained constant, heating through the dry layer or through the frozen layer results in equal drying rates and equal retention of volatiles. This indicates that the dry layer temperatures attained during the radiant heat transfer through the dry layer have no effect on the retention of volatile compounds. This effect is not unexpected, based on the results presented by Chirife and Karel (1974b) for heat stability of freeze dried carbohydrates.

When considering the effects of heating conditions, in which heat input is not controlled so as to maintain a constant ice front temperature, the possibility for increased loss of volatile occurs, especially if some collapse occurs. The contradictory retention behavior exhibited by various carbohydrates when heated at different heating plate temperatures (ice front temperatures were not monitored), as presented by Flink and Karel (1970b), is presumably due to the increasing extent of collapse in the glucose samples nullifying any improvement due to increased drying rate, while the noncollapsing sample (dextran) shows an increase in volatile.

(9) **Summary of Model System Studies.** Based on the volatile retention behavior observed in freeze drying model systems, it is seen that on a percentage retention basis the most important processing variables are: (1) ice front temperature; (2) freezing rate; (3) solids' concentration.

PROCESSING CONDITIONS AND FLAVOR RETENTION IN "REAL" FOODS

This section will be divided into two parts, one being short summaries of literature articles having flavor retention data for real foods, and the other being a more comprehensive presentation of two studies which have not been previously reported in the technical literature.

Table V. Retention of Volatile Compounds following Freeze Drying of Orange Juice and an Orange Juice Simulating Model Solution

	% retention				
		Dearomatized juice		Model solution	
	Natural juice	100 ppm	1000 ppm	100 ppm	1000 ppm
Ethanol	31	34	29	22	27
Butanol		51	47	27	48
Pentanol		52	56	31	34
Limonene	63	64	63		

Table VI. Retention of Volatile Compounds of Freeze Dried Orange Juice

	Retention, %		
	d-Limonene initial conen, %		
Heating plate temp, °F	0.011	0.046	Water-soluble volatiles
120	26	30	22
110	48	30	28
100	54	26	24
90	26	42	19
80	29	30	24
70	44		24

(1) **Apple Juice (Chandrasekaran and King, 1971).** Apple juice was freeze dried for a period of time which gave partial removal of the initial water (i.e., the material was not dry when the experiments were halted, still containing about 80% of the initial water). They observed that while the eutectic melting point is about −23°, the samples begin to show surface liquid at temperatures of −26°, thus causing termination of the drying. Four major regions of the vapor phase gas chromatogram were evaluated for flavor retention. In all cases, the volatile retention behavior improved as the initial solids content of the apple juice was increased from 17 to 36%. A further increase in solids to 44% showed no improvement over the retention at 36% solids. At the time of termination of the experiments, volatile retentions were determined and are shown in Table II.

(2) **Apple Slices (Saravacos and Moyer, 1968).** Freeze dried apple slices were reconstituted in water containing four volatile organic compounds and then re-freeze dried. The apple slices showed retention behavior very similar to that exhibited by low methoxy pectin gels, with retention levels dependent on the volatile species being considered.

(3) **Apricots (Lee et al., 1966a).** In a comparison of various methods for drying apricots, freeze drying was conducted using either slow (cabinet at −25°) or rapid (liquid nitrogen immersion) methods as the freezing treatment. Retention of flavor did not vary with freezing treatment and was approximately 91% as measured by volatile reducing substances and 93% as measured by volatile carbonyl compounds. Histological comparison of the fresh apricots and the two freeze dried samples showed that the liquid nitrogen frozen and dried samples had a cell structure almost unchanged from the fresh, while the slow frozen sample showed a disrupted cell structure due to ice crystal growth. It appears that this cellular disruption has no effect on flavor retention.

(4) **Banana Puree (Flink, 1970).** The influence of addition of sugar (16%) to banana puree on the retention of volatiles was noted in some preliminary thesis experiments. The results of these experiments showed that the more vol-

Table VII. Generalized Summary of Results Presented by Sauvageot et al. (1969)

Process parameter increased	Units	Values	General trend in retention	Exceptions
Chamber pressure	Torr	0.02 0.12	No change	None
Freezing rate	°C/min	0.5 6.6 16	Decreased retention	A few noted with orange juice
Frozen layer temp	°C	−26 −36	No change	Ethanol shows large decrease
Temp during desorption	°C	28 40 60	Raspberry juice: some loss when compare 28° to 60° Orange juice: no change between 25 and 45°	Acetaldehyde has sizable decrease
Duration of desorption	hr	9 7	Some decrease especially when dry at −36°	Acetaldehyde shows no effect
Thickness of frozen layer	mm	5 10	Slight decrease in retention	
Dry solids content	%	12 18	Retention increased	Acetaldehyde shows no change Ethanol decreased

Table VIII. Retention of Volatile Components of Freeze Dried Peach Slices

Treatment	Soluble solids content, %	Volatile reducing substances	Volatile carbonyls
Fast freezing	11.0	98	92
Slow freezing	11.6	94	92
Partial osmosis + slow freezing	17.0	103	127

tolerance of the dry layer to flavor changes was presented for conditions designed to give "no noticeable flavor loss" or "no significant flavor loss". With an ice front temperature of −25°, the dry layer should not be permitted above 93°. Some examples of maximum times at various temperatures are given in Table IV.

(6) **Onion Juice (Ofcarcik and Burns, 1974).** Pyruvic acid retention was determined for Bermuda onion juice with added carbohydrates, or with added mixtures of carbohydrates. They showed that addition of glucose, sucrose, or lactose gave improved retention up to 10% added solids; addition above this concentration gave very little improvement in pyruvic acid retention. When mixtures of sugars at a total solids concentration of 10% are added to the onion juice, no effect of added sugar composition was noted.

Table IX. Retention of Volatile Alcohols during Freeze Drying of Tomato Juice

Freezing conditions	Retention of alcohols, % ethanol–propanol–butanol at thickness, mm			
	3	5	7.5	10
−40° blast	7–11–14			41–57–63
−40° still air	15–23–27	27–40–47	39–58–64	40–53–63
Step program[a]	17–22–22	40–51–56		52–62–62

[a] −8, −20, −30, −40°.

Table X. Retention of Volatile Alcohols during Freeze Drying of Tomato Juice

Initial alcohol concn, %	% retention		
	Ethanol	Propanol	Butanol
0.1	52	62	62
0.01	39	40	41

Table XI. Increase in Solids Concentration due to Osmotic Pretreatment

Fruit	Solids concn, %	
	Before osmosis	After osmosis
Strawberries	9.4	23.0
Honeydew melon	9.6	33.6
Cantaloupe melon	9.6	28.0
Peaches	10.7	29.4
Pears	14.3	28.0
Pineapple	12.1	27.9
Apples	12.8	29.9

atile components were retained to a lower extent, that sugar addition had a greater effect on the less volatile species (2-pentanone and butanol) than on the more volatile species (ethanol, ethyl acetate, isobutyl acetate, and isoamyl acetate), and that flavor retention data were more variable when samples had added sugar.

(5) **Coffee (Ettrup-Petersen et al., 1973).** Influences of various freezing procedures (both rates and gas incorporation) and chamber pressures (ice front temperatures) were investigated for their effect on retention of flavor during freeze drying of coffee granules (Table III). The retention of flavor was improved by slow freezing and by freeze drying at the lowest ice front temperature. The influence of gas addition was dependent on the method used for incorporation. It was further demonstrated that sizable loss of flavor occurs when the ice front temperature is allowed to reach the collapse temperature.

Coffee (Hair and Strang, 1969). The time-temperature

(7) **Orange Juice (Voilley et al., 1973).** Retention of a number of flavor compounds was determined for natural orange juice, dearomatized orange juice with added volatiles, and a model solution with added volatiles. When the added volatiles were present initially at either 1000 or 100 ppm, in the dearomatized juice, the percentage retention was the same. This contrasts with the behavior observed for the model system where they found that the percentage retention decreased as the initial volatile concentration decreased. The natural juice showed retention behavior similar to that observed with the dearomatized juice. Some typical results are shown in Table V.

Orange Juice (Massaldi and King, 1974b). Measurements of *d*-limonene retention for freeze dried orange juice showed an apparent influence of *d*-limonene solubility and subsequent stabilization of the insoluble *d*-limonene droplets by "cloud particles." With increasing initial *d*-limo-

Table XII. Sample Scores for Difference Tests for Taste Acceptability

Sample no.	Fruit	Organoleptic scores[a]			
		IS	IF	NS	NF
1	Cherries	3.18	3.00	3.36	3.29
2	Honeydew	3.63	3.27	3.63	3.13
3	Cantaloupe	4.77	4.08	3.92	4.00
4	Strawberries	3.93	3.79	4.21	3.57
5	Cantaloupe	4.50	3.95	3.84	
6	Strawberries	4.42	4.12	3.79	3.42
7	Cantaloupe (rehydrated)	3.42	2.92	3.29	2.50
8	Pears	4.65	3.60	3.90	3.90
9	Peaches	4.25	3.50	2.83	2.42
10	Pineapple	4.37	3.75	3.50	2.42
11	Pears	3.75	3.10	3.55	4.20
12	Apples	4.58	3.75	2.62	2.58
13	Apples (rehydrated)	4.69	4.00	2.85	

[a] 6 = excellent, 1 = very poor.

Table XIII. Sample Scores from Ranking Tests[a]

Sample no.	Fruit	Rank			
		First	Second	Third	Fourth
1	Cherries	NS	IS	IF	NF
		0.190	0.160	0.130	−0.140
2	Honeydew	NS	IS	NF	IF
		0.300	0.260	−0.037	−0.530
3	Cantaloupe	IS	NS	NF	IF
		0.675	0.023	−0.274	−0.408
4	Strawberries	IS	NS	NF	IF
		0.380	0.095	−0.095	−0.380
5	Cantaloupe	IS	NS	IF	
		0.492	−0.224	−0.268	
6	Strawberries	IS	NS	IF	NF
		0.737	0.161	−0.211	−0.687
7	Cantaloupe (rehydrated)[b]	IS	NS	IF	NF
		0.333	0.122	0	−0.454
8	Pears	IS	NF	NS	IF
		0.678	−0.060	−0.206	−0.412
9	Peaches	IS	IF	NS	NF
		0.969	−0.001	−0.233	−0.726
10	Pineapple	IS	IF	NS	NF
		0.687	0.172	0.111	−0.926
11	Pears	NF	IS	NS	IF
		0.618	0.326	−0.266	−0.678
12	Apples	IS	IF	NF	NS
		1.03	0.250	−0.518	−0.787

[a] The extreme values of ranking ± 1.03; solids content: N, normal; I, increased; freezing rate: S, slow; F, fast. [b] Only three samples giving maximum range of ±0.85 ⟵ 0 ⟵ (−0.85).

ORIGINAL PAGE IS OF POOR QUALITY

nene content, samples with cloud showed improved retention while samples without cloud had sizable decreases in retention.

Orange Juice (Berry and Proscher, 1969). The retention of *d*-limonene and water soluble volatiles was investigated as a function of initial *d*-limonene concentration and freeze dryer heating plate temperature. A summary of their results is presented in Table VI. It appears that for each volatile, there is some optimal heating plate temperature, though in some cases the variation is not too great.

Orange Juice (Sauvageot et al., 1969). The influence of a variety of process variables on the retention of a number of flavor compounds of orange juice and raspberry juice is summarized in Table VII. These results conform with few exceptions to those noted with model systems.

(8) **Peaches (Lee et al., 1966b).** Peach slices were freeze dried following fast freezing (liquid nitrogen immersion), slow freezing (cabinet at −25°), and partial osmosis followed by slow freezing. The retention of volatiles, which was measured as volatile reducing substances and volatile carbonyl compounds, is presented in Table VIII. It can be seen that freezing rate had little effect on retention of the volatile compounds. The authors postulate that the greater than 100% retention with the osmotic treatment may result from fragmentation of reducing sugar during dehydration.

(9) **Raspberry Juice (Sauvageot et al., 1969).** The influence of a variety of process variables on the retention of a number of flavor compounds of raspberry juice is summarized in Table VII (this is the same table as noted in section 7 above).

The remainder of this paper will present results of two previously unpublished studies on flavor retention in tomato juice and fruit slices.

Tomato Juice: Retention of Flavor Compounds in Freeze Dried Tomato Juice. In a study conducted by Mr. Mogens Granborg at the Food Technology Laboratory of the Technical University of Denmark while this author was a Guest Professor at that institution, the influence of a number of process variables on retention of flavor compounds of tomato juice was investigated.

In the first part of the study, three alcohols (ethanol, propanol, and butanol, each at 0.1% w/v) were added to canned tomato juice having a solids' concentration of 7%. The results are presented in Table IX. A number of observations of interest can be noted. The most striking improvement in retention of flavor results from increasing the sample thickness, a finding quite to the contrary of those noted in model system studies. This might, however, be due to slower freezing of the thicker samples. In agreement with model system studies, the slower the freezing rates, the better the retention. Lastly, in almost all cases, the retention increases with an increasing number of carbons in the volatile molecule. In one case, a comparison of retentions in 10 mm thick samples frozen by the step program was conducted for volatiles at initial concentrations of either 0.1 or 0.01% each. The results, shown in Table X, indicate that retention was higher at the higher initial alcohol concentration.

Fruit Slices. In model system studies, it was demonstrated that product flavor quality depended primarily on the initial solids' content and rate of freezing, if freeze drying was conducted so that matrix structural changes were avoided. In recent studies, experiments were conducted to determine if these same processing variables were significant in determining flavor quality of solid foods.

The initial solids' content was increased by an osmotic pretreatment. Sliced fruit was placed in a stirred 60% sucrose solution for a period of up to 6 hr. During this period water was lost by the fruit tissue due to differences in osmotic pressure. Some sugar was taken up by the surfaces of the fruit, but most was removed by a short (30 sec) rinse prior to freezing. The rinse was necessary to prevent sticki-

Table XIV. Summarized Significant Results for Organoleptic Tests of Freeze Dried Fruits[a]

Sample no.	Fruit	Difference test taste, %	Preference test		Ranking test, % (preferred is first)
			Preference[b]	Significance, %	
1	Cherries	NSD	NS/NF 8/14	NSD	NSD
			NS/IS 8/14	NSD	
			IS/IF 10/14	NSD	
2	Honeydew	NSD	IS/IF 13/15	1	IS/IF, 1
			NS/NF 11/15	NSD	NS/IF, 1
			IS/NS 8/15	NSD	
3	Cantaloupe	NS/IS, 1	IS/IF 11/13	5	IS/IF, 1
		IF/NF, 5	IS/NS 11/13	5	IS/NF, 1
		IS/NF, 5	NS/NF 7/13	NSD	IS/NS, 5
4	Strawberries	NSD	IS/IF 10/14	NSD	IS/IF, 5
			NS/NF 8/14	NSD	
			NS/IF 8/14	NSD	
5	Cantaloupe	IS/NS, 5	IS/NS 14/19	NSD	IS/IF, 1
			IS/IF 15/19	5	IS/NS, 1
6	Strawberries	NF/IS, 1	IS/NF 10/12	5	IS/NF, 1
		NF/IF, 1	IS/NS 10/12	5	IS/IF, 1
		NS/IS, 5	NS/NF 9/12	NSD	IS/NF, 1
7	Cantaloupe (rehydrated)	NSD	NS/NF 9/12	NSD	IS/NF, 5
			IS/NS 8/12	NSD	
			IS/IF 8/12	NSD	
8	Pears	IS/IF, 5	IS/NS 7/10	NSD	IS/IF, 1
			NS/NF 5/10	NSD	IS/NS, 1
			IS/IF 8/10	NSD	IS/NF, 5
9	Peaches	IS/NS, 1	IS/IF 11/12	1	IS/IF, 1
		IS/NF, 1	NS/NF 9/12	NSD	IS/NS, 1
		IF/NF, 1	IS/NS 12/12	0.1	IS/NF, 1
		IF/NS, 5			IF/NF, 1
		IS/IF, 5			NS/NF, 5
10	Pineapple	NF/NS, 1	IS/IF 8/12	NSD	IS/NS, 1
		NF/IF, 1	IS/NS 7/12	NSD	IS/NF, 1
		NF/IS, 1	IS/NF 11/12	1	IF/NF, 1
		IS/NS, 5			NS/NF, 1
					IS/IF, 5
11	Pears	NF/IF, 1	NF/NS 8/10	NSD	NF/IF, 1
			IS/NS 8/10	NSD	NF/NS, 1
			IS/IF 9/10	5	IS/IF, 1
					IS/NS, 5
12	Apples	IS/NF, 1	IS/IF 12/12	0.1	IS/NS, 1
		IS/NS, 1	NF/NS 8/12	NSD	IS/IF, 1
		IF/NF, 1	IS/NS 12/12	0.1	IS/NF, 1
		NS/IF, 1			IF/NS, 1
		IS/IF, 1			IF/NF, 1
					NS/NF, 5
13	Apples (rehydrated)	NS/IS, 1	IS/NS 13/13	0.1	
		NS/IF, 1	IS/IF 12/13	1	
		IS/IF, 5			

[a] Normal solids/slow freezing, NS; normal solids/fast freezing, NF; increased solids/slow freezing, IS; increased solids/fast freezing, IF.
[b] Number of judges preferring a given treatment/total number of judges.

ORIGINAL PAGE IS
OF POOR QUALITY

ness of the dehydrated product. Table XI gives the increase of initial solids' concentration for a number of the fruits listed. In almost all cases, the contribution of added sugar is about 4%.

Samples were either slowly frozen in a −20° chamber or rapidly frozen by immersion in liquid nitrogen. Samples were freeze dried at ambient plate temperature and chamber pressure below 0.1 Torr.

The four samples produced were encoded as follows: IS, increased solids, slow frozen; IF, increased solids, fast frozen; NS, normal solids, slow frozen; NF, normal solids, fast frozen. Three methods of organoleptic testing were utilized in evaluating the relative quality of the different processing conditions for a number of fruit products.

Products were scored in a difference test for taste and texture using the following scale (together with numerical equivalents): very poor (1), poor (2), fair (3), good (4), very good (5), and excellent (6). By analysis of variance, the differences between samples were evaluated for significance. In addition, the average value of the scores can be used as a measure of product acceptability.

A second test was a paired comparison preference test in which samples were presented in groups of two. In this case, the judge merely expresses a preference for one sam-

Table XV. Summarized Relative Evaluation of Quality

Sample no.	Fruit	Preference tests	Ranking
1	Cherries	NS > NF, IS > IF	NSD
2	Honeydew	IS > NS > (?) IF > NF	NS, IS
3	Cantaloupe	IS > IF, NF, NS	IS
4	Strawberries	IS > (?) NS > (?) NF, IF	IS
5	Cantaloupe	IS > NS > IF	IS
6	Strawberries	IS > NS, IF > NF	IS
7	Cantaloupe (rehydrated)	IS > IF, NS > NF	IS
8	Pears	IS > NS, IF, NF	IS
9	Peaches	IS > NF > IF, NS	IS
10	Pineapple	IS, NS, IF > NF	IS
11	Pears	IS, NF > NS, IF	IS, NF
12	Apples	IS > NF, IF > NS	IS
13	Apples (rehydrated)	IS > IF, NS	

ple over the other. By consideration of the various combinations of paired comparisons, an overall preference can be determined.

In the third organoleptic test, all samples were presented for ranking according to overall quality. By analysis of variance an evaluation of ranking significance can be made. For most tests, when four samples were presented, the degree to which the sample score approaches +1.03 is a measure of its overall acceptance and the difference between values is a measure of the degree of preference.

The results of the organoleptic evaluations are presented in a series of tables (XII–XV).

The scores of the difference tests are presented in Table XII and numerical evaluations of ranking preference tests are given in Table XIII. The highest scores for taste are given in almost all cases to the increased solids, slow frozen (IS) fruits. The notable exception is with cherries where all the samples have a "fair" rating. In most cases, the IS fruits have rated above 4.0 for taste, with a number of samples in the "very good" range (above 4.5). The ranking preference tests (Table XIII) also demonstrate the clear superiority of the IS fruits. Evaluations of statistical significance of the various organoleptic tests are shown in Table XIV, these being summarized in Table XV. These data demonstrate the superiority of the IS fruits.

CONCLUSION

It has been shown through studies using model systems and real foods that the retention of flavor quality during freeze drying is dependent on the process conditions chosen. In most cases, the retention behavior exhibited by the model system studies, and predicted by the currently accepted mechanistic interpretations of freeze drying flavor retention, is also observed with real foods. In particular, the most important process condition appears to be drying so that matrix structure remains unaltered. If this condition is met, the most important process variables are initial solids content and freezing rate. It has been demonstrated that by proper control of the process parameters, retention of flavor compounds can be increased by factors of 2–3.

LITERATURE CITED

Bellows, R. J., King, C. J., *AIChE Symp. Ser. No. 132*, **62**, 33 (1973).
Berry, R. E., Froscher, J. L., *Proc. Fla. State Hortic. Soc.* **82**, 221 (1969).
Chalmers, R. A., Watts, R. W. E., *Analyst* **97**, 224 (1972).
Chandrasekaran, S. K., King, C. J., *Chem. Eng. Prog. Symp. Ser. No. 108*, **67**, 122 (1971).
Chandrasekaran, S. K., King, C. J., *AIChE J.* **18**(3), 513 (1972a).
Chandrasekaran, S. K., King, C. J., *AIChE J.* **18**(3), 520 (1972b).
Chirife, J., Karel, M., *J. Food Sci.* **38**, 768 (1973a).
Chirife, J., Karel, M., *J. Agric. Food Chem.* **21**, 936 (1973b).
Chirife, J., Karel, M., *Cryobiology* **11**, 107 (1974a).
Chirife, J., Karel, M., *J. Food Technol.* **9**, 13 (1974b).
Chirife, J., Karel, M., Flink, J., *J. Food Sci.* **38**, 671 (1973).
Ettrup-Petersen, E., Lorentzen, J., Flink, J., *J. Food Sci.* **38**(1), 119 (1973).
Flink, J., presented at the 6th International Course on Freeze Drying and Advanced Food Technology, Burgenstock, Switzerland, 1973 (proceedings to be published in 1975).
Flink, J. M., Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1970.
Flink, J., Gejl-Hansen, F., *J. Agric. Food Chem.* **20**(3), 691 (1972).
Flink, J. M., Gejl-Hansen, F., Karel, M., *J. Food Sci.* **38**, 1174 (1973).
Flink, J., Karel, M., *J. Food Technol.* **7**, 199 (1972).
Flink, J. M., Karel, M., *J. Agric. Food Chem.* **18**, 295 (1970a).
Flink, J. M., Karel, M., *J. Food Sci.* **35**, 444 (1970b).
Flink, J. M., Labuza, T. P., *J. Food Sci.* **37**, 617 (1972).
Fritsch, R., Mohr, W., Heiss, R., *Chem.-Ing.-Tech.* **43**(3), 445 (1971).
Gejl-Hansen, F., Technical Chemistry Thesis, Technical University of Denmark, 1971 (in Danish).
Hair, E. R., Strang, D. A., U.S. Patent 3,486,907 (1969).
Karel, M., Flink, J. M., *J. Agric. Food Chem.* **21**(1), 16 (1973).
King, C. J., "Freeze-Drying of Foods", Chemical Rubber Publishing Co., Cleveland, Ohio, 1971.
King, C. J., Chandrasekaran, S. K., *Prog. Refrig. Sci. Technol., Proc. Int. Congr. Refrig., 12th, 1967*, **3**, 649–656 (1973).
Lee, C. Y., Salunke, D. K., Nury, F. S., *J. Sci. Food Agric.* **17**, 393 (1966a).
Lee, C. Y., Salunke, D. K., Watters, G. G., Nury, F. S., *Food Technol.* **20**, 845 (1966b).
Maier, H. G., *Naturwissenschaften* **55**(4), 180 (1968).
Maier, H. G., *Z. Lebensm.-Unters.-Forsch.* **144**(1) (1970).
Maier, H. G., Bauer, A., *Die Starke* **24**(4), 101 (1972).
Massaldi, H. A., King, C. J., *J. Food Sci.* **39**, 438 (1974a).
Massaldi, H. A., King, C. J., *J. Food Sci.* **39**, 445 (1974b).
Menting, L. C., Hoogstad, B., *Experientia* **23**(9), 738 (1967).
Ofcarcik, R. P., Burns, E. E., *J. Food Sci.* **39**, 350 (1974).
Rey, L. R., Bastien, M. C., *Freeze-Drying Foods, Proc. Conf. 1961*, 25–42 (1962).
Rulkens, W. H., Thijssen, H. A. C., *J. Food Technol.* **7**(1), 79 (1972).
Saravacos, G. D., Moyer, J. C., *Chem. Eng. Prog. Symp. Ser. No. 86*, **64**, 37 (1968).
Sauvageot, C., Beley, P., Marchand, A., Simatos, D., Symposium on Surface Reactions in Freeze-Dried Systems, Commission X of the International Institute of Refrigeration, Paris, Dec 11–12, 1969.
Thijssen, H. A. C., *J. Appl. Chem. Biotechnol.* **21**(12), 372 (1972a).
Thijssen, H. A. C., *Proc. Nord. Aroma Symp., 3rd, 1972* (1972b).
Thijssen, H. A. C., presented at the 6th International Course on Freeze Drying and Advanced Food Technology, Burgenstock, Switzerland, 1973 (proceedings to be published in 1975).
Thijssen, H. A. C., Rulkens, W. H., *Ingenieur* **80**(47), 45 (1968).
Thijssen, H. A. C., Rulkens, W. H., "Effect of Freezing Rate on Rate of Sublimation and Aroma Retention in Freeze-Drying", presented at Lausanne, Switzerland, June 5–7, 1969 (1969a).
Thijssen, H. A. C., Rulkens, presented at the CHISA Conference, Marienbad, Czechoslovakia, Sept 15–20, 1969 (1969b).
Voilley, A., Sauvageot, F., Simatos, D., *Prog. Refrig. Sci. Technol., Proc. Int. Congr. Refrig., 13th* **3**, 639–647 (1973).

Received for review January 22, 1975. Accepted April 11, 1975. The studies on fruit slices were supported by Contract No. 9-12485 with NASA/MSC, Houston, Tex. Presented at the Symposium on Flavor Chemistry of Processed Foods, 168th National Meeting of the American Chemical Society, Division of Agricultural and Food Chemistry, Atlantic City, N.J., Sept 1974.

Theoretical approach to choosing process conditions giving optimal flavor quality in freeze-dried foods

M. Karel and J. M. Flink

Department of Nutrition and Food Science
Massachusetts Institute of Technology
Cambridge, Mass. 02139, USA.

ABSTRACT

Research on model systems has resulted in the formulation of a theory of retention of organic volatiles, including flavor, in freeze dried systems. The model systems studied included sugars, polysaccharides and proteins. The results in all of the systems conform to the predictions of a theory explaining most of the retention as due to entrapment in microregions.

The "microregion theory", as well as the "selective diffusion" theory allow the prediction of optimal process conditions for maximizing flavor retention. The process variables, the influence of which is predicted by theory, include:

A. Solids composition and concentration
B. Freezing rate
C. Sample dimensions
D. Frozen layer temperature or chamber pressure
E. Heat input conditions

In addition, in formulated systems the volatile concentration may be controlled, and the composition as well as total concentration of the solids may be varied, and has an effect on retention. The theory allows prediction of effects of composition and environmental factors such as humidity and temperature on stability of the freeze dried systems in storage.

The present paper illustrates the above principles through evaluation of selected results obtained in model systems.

I. INTRODUCTION

After many years of being considered a small scale specialty operation, freeze-drying has "come-of-age" with the great market success of freeze-dried coffee. It can be expected that this success will lead to future growth in other areas such as dehydrated tea extracts and fruit juices. Basically, all these products are aqueous solutions of soluble carbohydrate materials. Particularly important as a quality parameter is the distinctive flavor associated with each product. It is generally accepted that the flavor of a food material is composed of a complex mixture of hundreds of organic compounds, each present in the flavor mixture in minute concentration. At present, over 400 organic compounds have been identified as present in coffee extract. To what extent each of the many flavor compounds actually is important in producing the characteristic aroma of the particular product is not known; however the more volatile members of the alcohols, esters, carbonyls, and acids, are certainly quite important.

Freeze-drying, which has been recognized as a gentle preservation process due to the low temperatures at which drying occurs, has been used for many years for dehydration of sensitive biological materials, such as pharmaceuticals and enzymes. For those food materials which are essentially aqueous solutions, product quality depends mainly on the influence of the freeze-drying process on the quantity of aroma molecules retained by the dried solute. Many of the organic compound present in the food aroma have vapor pressures (i.e. in the pure state) higher than that of water. While the influence of the freezing process on the partial pressure of these volatiles in the food liquid is not well understood, the volatile partial pressure in the frozen solution can be sizable when compared to the partial pressure exerted by the ice present in the frozen material.

ORIGINAL PAGE IS
OF POOR QUALITY

Interest in freeze-drying of liquid food materials in the past few years has led to a number of investigations into the factors affecting the retention of volatile organic compounds during the freeze-drying of aqueous solutions. Some studies have resulted in development of mechanisms by which observed volatile retention phenomena may be explained. At present, two approaches appear to give good mechanistic descriptions for observed volatile retention phenomena. These have been labeled the "selective diffusion" and "microregion entrapment" theories. While these appear to be based on fundamentally different approaches, it is likely that they are partial explanations of the same phenomena though at different levels of analysis. "selective diffusion" being a mathematical macroscopic view, "microregion entrapment" being a morphological microscopic view.

II. THE "MICROREGION" THEORY

The essential features of the microregion theory are:

1) Interaction of non-volatile solutes which form a matrix, entrapping the volatiles. The integrity of this matrix is necessary for retention of volatiles. The evidence for the importance of this matrix was demonstrated by experiments in which the matrix structure was disrupted by thermal treatments, or by sorption of water or of polar volatiles (Chirife and Karel, 1974b; Flink and Karel, 1972). The extent to which matrix disruption is effective in releasing volatiles is shown in Table 1.

2) Volatile retention regions are quite small, being on a microscale. This was demostrated in experiments showing grinding and other mechanical treatments do not substantially reduce volatile retention (Flink and Karel, 1970a).

3) Volatiles of limited solubility are retained in the form of liquid droplets (Flink et al, 1973; Flink and Gejl-Hansen, 1972). The droplets can be visualized by various microscopic techniques. A typical micrograph is shown in Figure 1.

Mechanistically, the volatile retention phenomena can be described as follows:

1) Prior to freezing, volatile organic constituents of the aqueous model system exist in the liquid state as a molecular dispersion or liquid droplets depending on the relative levels of concentration and volatile solubility. The carbohydrate molecules are fully hydrated and there are no carbohydrate-carbohydrate or carbohydrate-volatile interactions.

During the lowering of temperature accompanying freezing, solubility limits of some of the volatiles present initially as molecular dispersion may be exceeded and droplets form. Other will remain as molecular dispersions.

2) During freezing, crystallization of water will result in continuous concentration of the unfrozen solution between the growing ice crystals. Volatile molecules will be in the concentrated solute phase, even if droplets have formed due to limited solubility.

The volatile, as molecules or droplets, will be pushed by the growing ice crystals until they are trapped in the solute phase. The degree of incorporation of volatile in the solute phase will depend on freezing rate (relative rates of diffusion of volatile and of solute from ice crystal interfaces), the relative solubility of the volatile in the solute and in the interface region, and the presence and size of the volatile droplets.

The lowering of concentrated solute phase moisture content due to crystallization, results in molecular association of carbohydrate molecules due to hydrogenbonding. This association produces a complex structure which acts to entrap both molecularly dispersed volatile and droplets of volatiles. The extent of organization of microregion structure and thus its effectiveness in entrapment depends on many factors, such as freezing conditions, concentration of matrix-forming solute and temperature. The degree of inclusion of volatile in the matrix appears to follow a definite relationship between volatile carbon chain length (probably a measure of volatile solubility) and carbohydrate molecule size (probably a measure of matrix organizational capacity).

ORIGINAL PAGE IS
OF POOR QUALITY

3) The ease of incorporation of volatile in the matrix and the degree of inter-carbohydrate associations by H-bonding determines the maximum extent of volatile retention during freeze-drying. These factors relate directly to structure formation in the matrix during freezing. The stabilization and maintenance of the previously developed structures is essential for the retention of vola ile during freeze-drying. This stabilization occurs due to increased intercarbohydrate H-bonding which accompanies the removal of water with the passage of the freeze-drying front.

The influence of processin parameters on freezedrying flavor retention are explained by their effect on microregion structure integrity.

III. EFFECT OF PROCESS CONDITIONS ON FLAVOR RETENTION

The "microregion theory", as well as the "selective diffusion" theory of Thijssen and coworkers, and that of King and coworkers, allow the prediction of optimal process conditions for maximizing flavor retention. The process variables, the influence of which is predicted by theory, include:

A. Solids composition and concentration
B. Freezing rate
C. Sample dimensions
D. Frozen layer temperature or chamber pressure
E. Heat input conditions.

A. Solids composition and concentration

The influence of the type of solid component on volatile retention has been demonstrated in almost all model system studies published, though direct comparison between studies is hazardous due to the variation of other process parameters. Flink and Karel (1970b) presented a tabulation of the retention of various volatile compounds by a variety of mono-, di- and polysaccharides freeze-dried under "identical" conditions. In this case, for most volatiles studied the disaccharides were the most effective, the monosaccharide next, followed by the polymer. In other studies (Chirife and Karel, 1974a) proteins were shown to be effective solids for retention of volatile components.

Studies on binary solid systems at a fixed total solids concentration have shown variable results (Ofcarcik and Burns, 1974; Flink, 1970). For some mixtures retention has improved in a synergistic manner, while in others no synergistic effects are noted. It seems likely that this variable behavior is related to the influence of the substituted species on the resultant structural stability of the freeze-drying matrix ("collapse"). Thijssen (1972) has shown how the retention of propanol decreases as glucose is substituted for maltodextrin when freeze drying at an ice front temperature of -25°C.

Synergistic effects may result from changes in matrix properties if freezing results in different phase structures of the matrix. Gejl-Hansen (1971) observed freeze-dried mixed maltose/maltodextrin systems microscopically. At intermediate levels of maltose substitution, the "dendritic" matrix structure changed to a "cubic cellular" appearance, though eventually, at higher levels of maltose substitution, the dendritic structure reappeared. Unfortunately, volatile retention behavior was not evaluated.

Many researchers have noted the importance of the initial solids concentration on the retention of volatile compounds during freeze drying. Chirife et al (1973) and Thijssen (1973) have presented information showing that, at low solids concentrations (bellow 10-20%), increases in solids concentration greatly increases volatile retention. When the initial solids concentration is greater than about 25%, there is little effect of further increases on volatile retention. The initial solids concentration at which volatile retention attains its asymptotic value appears to depend on the volatile species and solid species present in the model system.

If the above observations are considered on a unit weight of solids basis, it is seen that there exists an optimum solids concentration at which the volatile retained per unit of solids is a maximum. This optimum will be lower than the solids concentration at which the volatile retention reaches its asymptote.

ORIGINAL PAGE IS
OF POOR QUALITY

B. Freezing rate

As explained previously, the rate of freezing will influence the structure of the freeze-dried material as it controls the size of the ice crystals and the degree of solute concentration achieved in the matrix phase. The rate of freezing is one of the most investigated process variables and in all cases, slow freezing results in improved retention of the volatile components. Volatile rentention after slow freezing has been observed to be 2 to 3 times greater than after rapid freezing (Chirife and Karel, 1974). Table 2 shows the magnitude of the freezing rate effect for several systems.

C. Sample dimensions

The influence of the sample dimensions has been reported for slabs (Chirife et al, 1973) and for layers of granules (Thijssen, 1972). Sample dimensions which result in improvements in drying rate (thinner slabs or thinner layers of granules) generally will give increased retention of the volatile.

The relationship of diameter of the individual granule to volatile retention is more complex, as there exists for any layer thickness a granule size at which volatile retention is optimum, even though drying rates decrease as the granule size increases (Rulkens and Thijssen, 1972). Since the optimal granule size increases as the freezing rate decreases, it appears that for small particles there is a relationship of total dimension and ice crystal dimension which is important relative to volatile retention.

D. Frozen layer temperature or chamber pressure

The influence of frozen layer temperature which in turn depends on chamber pressure (Karel, 1974), has already been alluded to above. Thijssen (1972) and Violley et al (1973) have shown that as the ice front temperature increases, the retention of volatile compounds decreases. Increases in ice fron temperature which do not result in collapse of the drying matrix will nevertheless result, according to the phase diagram, in a decrease of the matrix solids concentration due to the melting of some of the ice crystals. Collapse of the freeze drying matrix results in substantial loss of the volatile components, with the loss being directly related to the extent of collapse (Bellows and King, 1973).

E. Heat input conditions

Heat input to the sample will influence a number of factors, such as drying rate, temperature gradients, ice front temperature, etc. It has already been shown that drying rate will influence the retention of volatile compounds. Rulkens and Thijssen (1972) have shown that, if the ice front temperature is maintained constant, heating through the dry layer or throught the frozen layer results in equal drying rates and equal retention of volatiles. This indicates that the dry layer temperatures attained during the radiant heat transfer through the dry layer have no effect on the retention of volatile compounds. This effect is not unexpected, based on the results presented by Chirife and Kare (1974b) for heat stability of freeze dried carbohydrates.

If heat input is not controlled so as to maintain a constant ice front temperature, the possibility for increased loss of volatile occurs, especially if some collapse occurs. The contradictory retention behavior exhibited by various carbohydrates when heated at different heating platen temperatures as presented by Flink and Karel (1970b), is presumably due to the increasing extent of collapse in the glucose samples nullifying any improvement due to increased drying rate, while the non-collapsing sample (dextran) shows an increase in volatile.

ACKNOWLEDGEMENT

This work was supported in part by contract no. 9-12485 with National Aeronautics and Space Administration, Manned Spacecraft Center, Houston, Texas.

REFERENCES

Bellows, R.J. and King, C.J. 1973. Product collapse during freeze drying of liquid foods. AIChE Symp. Series No. 132, 62:33.

Chirife, J. and Karel, M. 1974a. Volatile retention during freeze drying of protein solutions. Cryobiology 11:107.

Chirife, J. and Karel, M. 1974b. Effect of structure disrupting treatments on volatile release from freeze dried maltose. J. Fd. Technol. 9:13.

Chirife, J., Karel, M. and Flink, J.M. 1973. Studies on mechanisms of retention of volatiles in freeze-dried food models: The system PVP-n-propanol. J. Fd. Sci. 38:671.

Flink, J.M. 1970. Loss or organic volatiles in freeze-dried carbohydrate solutions. Ph.D. Thesis, M.I.T., Cambridge, Mass.

Flink, J.M. and Gejl-Hansen, F. 1972. Retention of organic volatiles in freeze-dried carbohydrate solutions: Microscopic observations. J. Agr. Food Chem. 20 (3):691.

Flink, J.M. and Karel, M. 1970a. Retention of organic volatiles in freeze-dried solutions of carbohydrates. J. Agr. Food Chem. 18:295.

Flink, J.M. and Karel, M. 1970b. Effects of process variables on retention of volatiles in freeze-drying. J. Food Sci. 35:444.

Flink, J.M. and Karel, M. 1972. Mechanisms of retention of organic volatiles in freeze-dried systems. J. Fd. Technol. 7:199.

Flink, J.M., Gejl-Hansen, F. and Karel, M. 1973. Microscopic investigations of the freeze drying of volatile-containing model food solutions. F. Fd. Sci. 38:1174.

Gejl-Hansen, F. 1971. An introduction to the investigation of aroma retention in frozen and freeze-dried malto-dextrin: colorimetric and microscopic (in Danish). Technical Chemistry Thesis, Technical University of Denmark.

Ofcarcik, R.P. and Burns, E.E. 1974. Carbonyl retention in model system and bermuda onion juice during lyophilization. Effect of simple carbohydrates, binary carbohydrate mixtures and sucrose inversion. J. Fd. Sci. 39:350.

Rulkens, W.H. and Thijssen, H.A.C. 1972. Retention of volatile compounds in freeze-drying slabs of malto-dextrin. J. Fd. Technol. 7(1):79.

Thijssen, H.A.C. 1972. Effect of processing conditions in drying liquid foods on aroma retention. Proceedings of the 3rd Nordic Aroma Symposium. Hämeenlinna, Finland, June 6-8, 1972.

Thijssen, H.A.C. 1973. Effect of process conditions in freeze drying on retention of volatile components. Presented at the 6th International Course on Freeze Drying and Advanced Food Technology, Burgenstock, Switzerland. (proceedings to be published in 1975).

Voilley, A., Sauvageot, F. and Simatos, D. 1973. Coefficients de volatilete relative et retention au cours de la lyophilisation de quelques alcools. In: Proceedings of the XIII International Congress of Refrigeration, Volume 3: p. 639. Avi Publishing Co., Westport, Conn.

TABLE 1

Effect of matrix-disrupting treatment on release of entrapped volatiles

Treatment	Matrix material	Volatile	% of originally entrapped volatile released by treatment
Vacuum "desorption"			
82° C.	Maltose	1-Propanol	0
100° C.	Maltose	1-Propanol	80
50° C.	Bovine serum albumin	2-Propanol	0
106° C.	Bovine serum albumin	2-Propanol	0
Sorption of water vapor "at specified RH"			
11 % RH.	Starch	2-Propanol	8
75 % RH.	Starch	2-Propanol	95
11 % RH.	Polyvinylpyrrolidone	1-Propanol	8
52 % RH.	Polyvinylpyrrolidone	1-Propanol	82
32 % RH.	Bovine serum albumin	2-Propanol	10
75 % RH.	Bovine serum albumin	2-Propanol	82
20 % RH.	Maltose	2-Propanol	0
61 % RH.	Maltose	2-Propanol	66
Sorption of organic vapors			
Ethyl ether (1.0)*.	Maltose	1-Propanol	0
Benzene (1.0).	Maltose	1-Propanol	0
Aniline (1.0).	Maltose	1-Propanol	30
Methanol (0.17).	Maltose	1-Propanol	0
Methanol (0.75).	Maltose	1-Propanol	70
Ethanol (0.75).	Maltose	1-Propanol	0

* Activity of organic vapor (1.0 = saturated vapors).

TABLE 2

Propanol retention during freeze drying of 2 % (w/w) carbohydrate and polymers solutions

Solid	% Retention: Rapidly frozen samples Initial propanol	% Retention: Slowly frozen samples Conc. = 0.5-1.0 %
Maltose.	69.5	–
Maltose.	67.6	–
Malto-dextrin.	–	71
Glucose.	47.8	–
Glucose.	52.8	–
Starch.	21.0	–
PVP.	–	25.5
PVP.	9.8	24.0
Dextran 10.	7.5	–
Dextran 10.	4.2	–
Cellulose.	4.0	–
	Initial propanol	Conc. = 100-250 ppm
Dextran 10.	56	97
Maltose.	16	88
PVP.	–	58
Starch.	38	–
Cellulose.	8.4	–

ORIGINAL PAGE IS OF POOR QUALITY

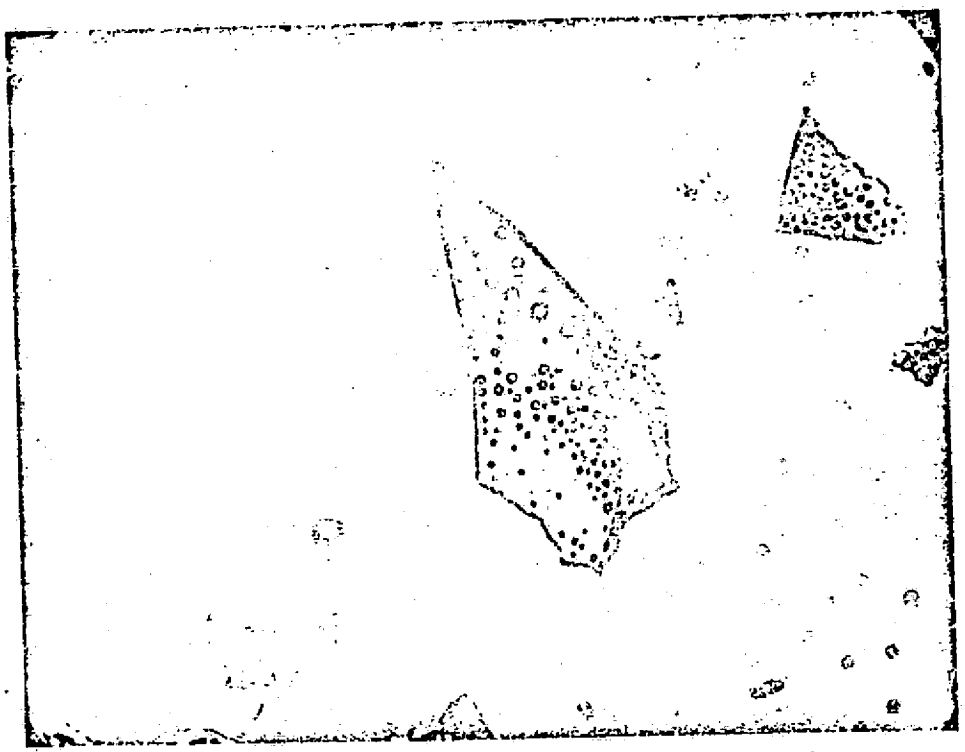


Fig. 1.–2-butanol droplets in a freeze-dried maltodextrin – 2-butanol system. Magnification 600 x. Initial concentrations in aqueous solution: 2-butanol 4 %, maltodextrin 15 %.

ORIGINAL PAGE IS
OF POOR QUALITY

Effect of processing conditions on quality of freeze dried foods

J. Flink and M. Karel

Dept of Nutrition and Food Science
Massachusetts Institute of Technology
Cambridge, Mass. 02139, USA.

ABSTRACT

Theoretical work on model systems has shown the major importance of some process conditions to retention of flavor during freeze drying. The applicability of these theoretical findings to design of processes for actual foods was evaluated. Two types of foods of present or potential commercial importance were studied: freeze dried fruits and freeze dried coffee solubles.

The fruits were studied in connection with development of food rations for space travel, but they would also be quite valuable in the commercial sector. The fruits included apples, pears, peach and melons, and others. The major processing factors varied were solids content and freezing rate. It was possible to achieve improved quality in all cases, as evaluated by organoleptic analysis using several procedures.

In the case of coffee, flavor retention as well as other important quality criteria were studied to determine the effect of the following process variables:

1. **Freezing rate**
2. **Chamber pressure**
3. **Incorporation of gas prior to freezing**

In general the results obtained with actual foods conforms to prediction formulated on the basis of initial work in model systems.

INTRODUCTION

Freeze drying is generally considered to be the dehydration process which will result in the highest quality dehydrated products. This is due to the fact that water is removed without the presence of a free liquid phase, and that heated regions in the dry layer have low moisture contents, while regions of high moisture have low temperatures. One of the crucial quality aspects, maintenance of product flavor, has aroused much interest in the recent past, as it was felt that flavor components, many of which are highly volatile, would be largely lost during the process since the freeze drying is generally conducted at absolute pressures of bellow 1 torr.

Most early studies on the retention of flavour during freeze drying have concentrated on simple model systems in which complications due to compositional variations of natural products could be avoided. By means of these studies, in which simple quantitative retention information could be easily evaluated and correlated with changes in process variables, two mechanistic interpretations of flavor retention phenomena during freeze drying were proposed. These were labelled the "selective diffusion" mechanisms (Menting and Hoogstad, 1967; Thijssen and Rulkens, 1968; King and Chandrasekaran, 1973) and the "microregion entrappment" mechanism (Flink and Karel, 1970a) by their respective proponents. It appears that there is some agreement that these two proposed mechanisms probably are describing the same basic phenomena from two different approaches, namely mathematical or macroscopic vs. morphological or microscopic viewpoints.

ORIGINAL PAGE IS
OF POOR QUALITY

In an earlier paper in this symposium, the basic properties of the "microregion entrappment" mechanism, by which flavor retention phenomena may be explained, have been presented. Based on these studies, process conditions have been specified by which flavor retention may be optimized. The true worth of these mechanisms, which have been conducted primarily with model systems, rests in their ability to predict processing conditions giving improved flavor quality for real food materials. The flavor retention behavior of a number of real food products, including both liquid coffee and solid foods (fruit pieces) have been evaluated. In most cases, flavor quality for the real food showed the same behavior relative to process conditions as predicted by the mechanisms base on model system studies.

Fruit Slices

Introduction: In model system studies, it was demonstrated that product flavor quality depended primarily on the initial solids content and rate of freezing, if freeze drying was conducted so that matrix structural changes were avoided. Experiments were conducted to determine if these same processing variables were significant in determining flavor quality of solid foods. Methods: The initial solids content was increased by an osmotic pretreatment. Sliced fruit was placed in a stirred 60% sucrose solution for a period of up to 6 hours. During this period water was lost by the fruit tissue due to differences in osmotic pressure. Some sugar was taken up by the surfaces of the fruit, but most was removed by a short (30 sec) rinse prior to freezing. The rinse was necessary to prevent stickiness of the dehydrated product. Table 1 gives the increase of initial solids concentration for a number of the fruits listed. In almost all cases, the contribution of added sugar is about 4%.

Samples were either slowly frozen in a -20°C chamber or rapidly frozen by immersion in liquid nitrogen. All samples were freeze dried under identical conditions.

The four samples produced were encoded as noted below:

IS	increased solids, slow frozen
IF	increased solids, fast frozen
NS	normal solids, slow frozen
NF	normal solids, fast frozen

Three methods of organoleptic testing were utilized in evaluating the relative quality of the different processing conditions for a number of fruit products.

Products were scored in a difference test for taste and texture using the following scale (together with numerical equivalents): very poor (1), poor (2), fair (3), good (4), very good (5) and excellent (6). By analysis of variance, the differences between samples were evaluated for significance. In addition, the average value of the scores can be used as a measure of product acceptability.

A second test was a paired comparison preference test in which samples were presented in groups of two. In this case, the judge merely expresses a preference for one sample over the other. By consideration of the various combinations of paried comparisons, an overall preference can be determined.

In the third organoleptic test, all samples were presented for ranking according to overall quality. By analysis of variance an evaluation of ranking significance can be made. For most tests, when four samples were presented, the degree to which the sample score approaches $+1.03$ is a measure of its overall acceptance and the difference between values is a measure of the degree of preference.

Results: The results of the organoleptic evaluations are presented in a series of Tables (2-5).

The scores of the difference tests are presented in Table 2, and numerical evaluations of ranking preference tests in Table 3. The highest scores for taste are given in almost all cases to the increased solids, slow frozen (IS) fruits. The notable exception is with cherries where all the samples have a "fair" rating. In most cases, the IS fruits have rated above 4.0 for taste, with a number of samples in the "very good" range (above 4.5). The ranking preference tests (Table 3) also demonstrate the clear superiority of the IS fruits. Evaluations of statistical significance of the various organoleptic tests are shown in Table 4 and 5, these being summarized in Table 6. These data demonstrate the superiority of the IS fruits.

Coffee Extract

Introduction: Production of instant coffee solubles by freeze drying is a well developed industry. Since the raw material, concentrated coffee extract is a liquid, the flavor retention behavior during freeze drying can be expected to follow quite closely the behavior noted with model systems. However, other product quality criteria (especially color and bulk density) are of importance and thus additional process variables are of concern. For this study, the influence of various freezing procedures (involving both rates and procedures for gas incorporation prior to freezing) and chamber pressures (ice front temperatures) were investigated for their effect on retention of flavor during freeze drying of coffee granules.

Methods: A single batch of coffee extract, adjusted to 28% solids was used for all experiments. Three freezing rates, classified as "very slow" (sequential 24 hour periods at -10, -20 and -40°C), "slow" (still air at -40°C) and "quick" (spray onto chilled drum at -52°C), were used. Some "slow" frozen samples had air whipped in prior to freezing and some "quick" frozen samples had CO_2 injected under pressure prior to spraying on the drum. (These treatments resulted in five basic freezing treatments as noted in Table 7). The frozen samples were granulated, and the 1.2 - 2.7 mm diameter fraction freeze-dried at chamber pressures from 0.2 to 0.8 torr (in 0.1 torr increments) until they reached constant weight. Heat input was limited so that the dry layer remained below 40°C.

Dry samples were reconstituted with water and following a strict regime, the headspace volatiles collected and analyzed by gas chromatography. Good reproductibilty was noted. Volatile retention was compared to the dry sample showing the highest quantity of volatile components in the headspace.

Results: Volatile retentions, expressed as a percentage of the highest sample area, are given in Table 7. Very slow and slow freezing resulted in much higher retentions of volatile compounds than quick freezing, as has been predicted by the mechanisms based on model system studies.

Although the chamber pressure shows little influence on volatile retention over the range of 0.3 - 0.7 torr, a large decrease in volatile retention occurs at a chamber pressure of 0.8 torr. Since the frozen-layer ice-front temperature can be assumed to be in equilibrium with the water vapor pressure in the chamber, because the small size of the granule reduces the pressure drop from the ice front to granule surface, coffee granules freeze dried at a chamber pressure of 0.7 torr have an ice front temperature of about -21°C, while samples freeze dried at 0.8 torr will have an ice front temperature of -20°C. Coffee extract has a collapse temperature of -20°C (Bellows, 1972). Thus, the large decrease in coffe volatiles at 0.8 torr reflects the changes in the structure of the freeze-dried matrix caused by collapse. The collapse phenomenon also greatly influences other quality parameters.

Foaming of the samples causes widely differing behavior, probably reflecting the differences in foaming methods. The samples which were slowly frozen showed considerable volatile loss due to the foaming. This was not surprising, since the extract was violently agitated in a soft ice machine for 5 min at 20°C with a large air headspace available for uptake of the volatile compounds.

The rapidly frozen samples, on the other hand, were foamed by injection of CO_2 into the liquid at a pressure above atmospheric. The extract was not agitated and no bubble surface area was formed until the pressure was released just prior to freezing. The rapid freezing also tended to stabilize the foam very rapidly before additional loss could occur.

ORIGINAL PAGE IS OF POOR QUALITY

TABLE 5

Sample		Difference Test	Preference Test		Ranking Test
		Taste	Preference*	Significance	(preferred is first)
8	Pears.	IS/IF 5 %	IS/NS 7/10	NSD	IS/IF 1 %
			NS/NF 5/10	NSD	IS/NS 1 %
		IS/NS 1	IS/IF 8/10	NSD	IS/NF 5 %
9	Peaches.	IS/NS 1 %	IS/IF 11/12	1 %	IS/IF 1 %
		IS/NF 1 %	NS/NF 9/12	NSD	IS/NS 1 %
		IF/NF 1 %	IS/NS 12/12	0.1 %	IS/NF 1 %
		IF/NS 5 %			IF/NF 1 %
		IS/IF 5 %			NS/NF 5 %
10	Pineapple.	NF/NS 1 %	IS/IF 8/12	NSD	IS/NS 1 %
		NF/IF 1 %	IS/NS 7/12	NSD	IS/NF 1 %
		NF/IS 1 %	NS/NF 11/12	1 %	IF/NF 1 %
		IS/NS 5 %			NS/NF 1 %
					IS/IF 5 %
11	Pears.	NF/IF 1 %	NF/NS 8/10	NSD	NF/IF 1 %
			IS/NS 8/10	NSD	NF/NS 1 %
			IS/IF 9/10	5 %	IS/IF 1 %
					IS/NS 5 %
12	Apples.	IS/NF 1 %	IS/IF 12/12	0.1 %	IS/NS 1 %
		IS/NS 1 %	NF/NS 8/12	NSD	IS/IF 1 %
		IF/NF 1 %	IS/NS 12/12	0.1 %	IS/NF 1 %
		NS/IF 1 %			IF/NS 1 %
		IS/IF 1 %			IF/NF 1 %
					NS/NF 5 %
13	Apples (rehydrated). ..	NS/IF 1 %	IS/NS 13/13	0.1 %	—
		NS/IF 1 %	IS/IF 12/13	1 %	
		IS/IF 5 %			

* Number of judges preferring a given treatment/total number of judges.

TABLE 6

Summarized relative evaluation of quality

Sample	Fruit	Preference tests	Ranking
1	Cherries.	NS > NF, IS > IF	NSD
2	Honeydew.	IS > NS > IF > NF	NS, IS
3	Cantaloupe.	IS > IF, NF, NS	IS
4	Strawberries.	IS > NS > NF, IF	IS
5	Cantaloupe.	IS > NS > IF	IS
6	Strawberries.	IS > NS, IF > NF	IS
7	Cantaloupe (rehydrated).	IS > IF, NS > NF	IS
8	Pears.	IS > NS, IF, NF	IS
9	Peaches.	IS > NF > IF, NS	IS
10	Pineapple.	IS, NS, IF > NF	IS
11	Pears.	IS, NF > NS, IF	IS, NF
12	Apples.	IS > NF, IF > NS	IS
13	Apples (rehydrated).	IS > IF, NS	—

Conclusion

It has been shown through studies using model systems and real foods, that the retention of flavor quality during freeze drying is dependent on the process conditions chosen. In most cases, the retention behavior exhibited by the model system studies, and predicted by the currently flavor mechanistic interpretations of freeze drying flavor retention, is also observed with real foods. In particular, the most important process condition appears to be drying so that matrix structure remains unaltered. If this condition is met, the most important process variables are initial solids content and freezing rate. It has been demostrated that by proper control of the process parameters, retention of flavor compounds can be increased by factors of 2-3

Acknowledgements

The studies on fruit slices were supported by Contract no. 9-12485 with NASA/MSC, Houston. The studies on coffee extract were conducted in co-operation with Atlas A/S of Copenhagen, Denmark and the Food Technology Laboratory of the Technical University of Denmark.

REFERENCES

Bellows, R. J. 1972. Freeze drying of liquid foods: Dependence of collapse temperature on composition and concentration. Ph. D. Thesis, University of California, Berkeley.

Flink, J. M. and M. Karel 1970. Retention or organic volatiles in freeze-dried solutions of carbohydrates. J. Agr. Food Chem. 18:295-297.

King, C. J. and S.K. Chandrasekaran 1973. Analysis of volatiles loss from food liquids during freeze-drying and evaporate drying as a ternary diffusion process. Proceedings of the XII International Congress of Refrigeration Volume 3, pp. 649-656, Avi Publishing Co., Westport, Conn.

Menting, L. C. and B. Hoogstad 1967. Selectivity of carbohydrate films as influenced by their moisture content. Experientia 23 (9): 738-740.

Thijssen, H.A.C. and W.H. Rulkens 1968. Retention of aromas in drying food liquids. De Ingenieur, 80(47):45-56.

ORIGINAL PAGE IS
OF POOR QUALITY

TABLE 1

Increase in solids concentration due to osmotic pretreatment

Fruit	Solids concentration (%)	
	Before osmosis	After osmosis
Strawberries	9.4	23.0
Honeydew melon	9.6	33.6
Cantaloupe melon	9.6	28.0
Peaches	10.7	29.4
Pears	14.3	28.0
Pineapple	12.1	27.9
Apples	12.8	29.9

TABLE 2

Sample Scores for Experience Tests for Taste Acceptability

Sample	Organoleptic Scores[a]			
	IS	IF	NS	NF
1. Cherries	3.18	3.00	3.36	3.29
2. Honeydew	3.63	3.27	3.63	3.13
3. Cantaloupe	4.77	4.08	3.92	4.00
4. Strawberries	3.93	3.79	4.21	3.57
5. Cantaloupe	4.50	3.95	3.84	—
6. Strawberries	4.42	4.12	3.79	3.42
7. Cantaloupe (rehydrated)	3.42	2.92	3.29	2.50
8. Pears	4.65	3.60	3.90	3.90
9. Peaches	4.25	3.50	2.83	2.42
10. Pineapple	4.37	3.75	3.50	2.42
11. Pears	3.75	3.10	3.55	4.20
12. Apples	4.58	3.75	2.62	2.58
13. Apples (rehydrated)	4.69	4.00	2.85	—

[a] 6 = excellent.
1 = very poor.

TABLE 3

Sample Scores from Ranking Tests

The extreme values of ranking ±1.03
Solids content: N: normal. I: increased
Freezing rate: S: slow, F: fast

Sample	Fruit	Rank			
		First	Second	Third	Fourth
1	Cherries.	NS	IS	IF	NF
		.190	.180	.130	−.140
2	Honeydew.	NS	IS	NF	IF
		.300	.260	−.037	−.530
3	Cantaloupe.	IS	NS	NF	IF
		.675	.023	−.274	−.406
4	Strawberries.	IS	NS	NF	IF
		.380	.095	−.095	−.380
5	Cantaloupe.	IS	NS	IF	—
		.492	−.224	−.268	
6	Strawberries.	IS	NS	IF	NF
		.737	.161	−.211	−.687
7	Cantaloupe (rehydrated. . . .	IS	NS	IF	NF
		.333	.122	0	−.454
8	Pears.	IS	NF	NS	IF
		.678	−.060	−.206	−.412
9	Peaches.	IS	IF	NS	NF
		.969	−.001	−.233	−.726
10	Pineapple.	IS	IF	NS	NF
		.687	.172	.111	−.926
11	Pears.	NF	IS	NS	IF
		.618	.326	−.266	−.678
12	Apples.	IS	IF	NF	NS
		1.03	.250	−.518	−.787

* Only three samples giving maximum range of + .85 — 0 — (-.85).

TABLE 7

Relative retention of coffee volatiles (based on total peak area) for various freezing and freeze-drying conditions

Freezing conditions[a]	Relative retention (%)[b] freeze-drying chamber pressure (torr)						
	0.2	0.3	0.4	0.5	0.6	0.7	0.8
Very slow.	92	96	78	77	66	67	34
Slow.	100	99	88	82	91	82	35
Foam, slow.	67	61	49	53	57	44	63
Quick.	47	53	38	38	44	35	36
Foam, quick.	48	—	42	42	43	32	29

[a] Very slow: stepwise to −40° C.
Slow: −40° C.
quick: spray onto chilled drum at −52° C.
[b] Relative to slow frozen sample dried at 0.2 torr.

ORIGINAL PAGE IS OF POOR QUALITY

TABLE 4

Summarized significant results for organoleptic tests of freeze dried fruits

	Normal Solids/Slow Freezing NS Normal Solids/Slow Freezing NF	Increased Solids/Slow Freezing IS Increased Solids/Fast Freezing IF		
		Preference Test		
Sample	Difference Test Taste	Preference*	Significance	Ranking Test (preferred is first)
1 Cherries.	NSD	NS/NF 8/14 NS/IF 8/14 IS/IF 10/14	NSD NSD NSD	NSD
2 Honeydew.	NSD	IS/IF 13/15 NS/NF 11/15 IS/NS 8/15	1 % NSD NSD	IS/IF 1 % NS/IF 1 %
3 Cantaloupe.	NS/IS 1 % IF/NF 5 % IS/NF 5 %	IS/IF 11/13 IS/NS 11/13 NS/NF 7/13	5 % 5 % NSD	IS/IF 1 % IS/NF 1 % IS/NS 5 %
4 Strawberries.	NSD	IS/IF 10/14 NS/NF 8/14 NS/IF 8/14	NSD NSD NSD	IS/IF 5 %
5 Cantaloupe.	IS/NS 5 %	IS/NS 14/19 IS/IF 15/19	NSD 5 %	IS/IF 1 % IS/NS 1 %
6 Strawberries.	NF/IS 1 % NF/IF 1 % NS/IS 5 %	IS/NF 10/12 IS/NF 10/12 NS/NF 9/12	5 % 5 % NSD	IS/NF 1 % IS/IF 1 % IS/NF 1 % IS/NS 5 % IF/NF 5 %
7 Cantaloupe (rehydrated).	NSD	NS/NF 9/12 IS/NS 8/12 IS/IF 8/12	NSD NSD NSD	IS/NF 5 %

5.3 Effect of Process Conditions on Osmotic Preconcentration of Freeze Dried Fruit

Tests have been conducted on the effectiveness of a variety of osmosis solutes at a number of process conditions for the osmotic preconcentration of apple slices prior to freeze drying. Apples were manually peeled and quartered and uniform slices cut from the quarters. All osmosis solutions contained (in addition to the osmotic agents) 0.52% ascorbic acid and 0.14% malic acid to prevent browning of the apple slices during handling and subsequent processing. Rates of osmosis have been measured gravimetrically by assuming that under the conditions used, solutes present in the apple slice will not diffuse against the total concentration gradient into the concentrated osmosis solution. The mass transport data is presented in Table 1.

5.3.1 Analysis of Mass Transport Data

The kinetic mass transport data from Table 1 can be analyzed according to standard techniques used for obtaining diffusion coefficients, assuming unsteady state Fickian diffusion to be occurring. Solutions to the unsteady state Fickian diffusion equation

$$\frac{dc}{dt} = D \frac{d^2c}{dx^2}$$

have been expressed by means of infinite series. By means of simplifying assumptions concerning the neqligible significance of higher order exponential terms, diffusion coefficients can be determined from graphical analysis of the kinetic data by the methods

of plotting either

$$\log \frac{C-C_{\infty}}{C_0 - C_{\infty}} \quad \text{vs. time} \qquad (1)$$

OR

$$C \text{ vs. } (\text{time})^{1/2} \qquad (2)$$

and measuring the slope of the resulting straight lines.

For the unsteady state Fickian diffusion model to exactly apply it is necessary that the test conditions be designed so that external solution concentrations remain constant, and that resistance at the surface is negligible compared to internal diffusion resistance. In the analysis presented here, it will be assumed that solution conditions remain essentially constant, though it is known that in the initial stages of the osmotic treatment, there is a sizable uptake of solute by the sample. Additionally, due to the osmotic loss of water from the sample, some dilution of the osmosis solution will occur. These changes are minimized by choosing a large volume of osmosis solution relative to the amount of apple slices being processed.

As will be noted in the results, the condition of total mass transfer resistance being internal to the piece is not met in a number of the tests, especially at higher concentrations of osmosis solution, and thus, the transport coefficients obtained are overall mass transport coefficients or pseudo "diffusion coefficients" rather than true coefficients of diffusion of water in apple tissue.

Several of the parameters measured in determing mass transport during osmosis can be used for the concentration terms of

equations 1 and 2. Figures 1-4 show four formats which were investigated for agitated osmosis with sucrose solutions. In figures 1-4 the particular concentration term is given as a function of time (i.e. as a measure of the course of the cummulative mass transport through the process) and as a function of square root of time (i.e. according to equation 2 above) where the slope is proportional to a mass transport factor.

Figure 1 gives the water lost per 100 grams of initial apple sample. It neglects the effect of solute uptake and does not account for differences of initial water contents of the various apple samples. This presentation presumably shows water diffusivity, though the changing apple solids content due to uptake of solute will alter the driving force for water flow beyond that due to the diffusive loss of water alone. Figure 2 gives the water lost on a unit initial water content basis. This is thus the fraction of initial water which has been lost. This format accounts for differences of initial water contents of the apple samples, but still does not account for changes in solids content due to solute uptake. Figure 3 gives the change in percent total solids. While this measure does not attempt to separate the solute uptake from the water loss, it measures a parameter of importance in this study, the increase of solids content prior to freeze drying. Figure 4 presents the percent total solids change on a unit initial total solids basis (i.e., normalized total solids), so that variations between initial samples can be considered.

Overall mass transport factors given by the slopes of the conventration vs $(time)^{1/2}$ curves are compared in Table 2. The absolute values are seen to vary depending on the units of concentration used. To permit comparisons, Table 2 also includes relative rates based on 40% sucrose having a rate of 1.00. (The choice of the 40% sucrose basis is dictated by the questionable data curve for 25% sucrose in Figure 2.) It can be seen that the relative rates are similar for the two concentration formats based on water, and for the two formats based on total solids, and that as expected, the trends are the same for all the formats.

The mass transport factors, which are obtained from the slope of the normalized % total solids vs $(time)^{1/2}$ curve are overall coefficients which include a factor related to concentration and a combination of factors which are ideally independent of concentration. In the case of this study, the concentration factor is the normalized solids content (in percent) which would exist at infinite osmosis time. This equilibrium concentration will be a function of the osmosis solution concentration. To test if the mass transport factors can be considered to have the form

$$MTF = KC_{\infty}$$

where MTF = mass transport factors

K = mass transport coefficient which ideally is independent of concentration

C_{∞} = normalized % solids content in sample at infinite time

C_∞ values were approximated from C vs t curves and K values calculated. The results, shown in Table 3, indicate that the K values are not independent of concentration. The increase in K value with concentration is seen to be greater for agitated systems than for non-agitated.

With the data available at this time, it is not possible to conclusively identify the reasons for the differences between agitated and non-agitated systems, and for the rise in mass transport coefficient with sucrose concentration for the agitated system. Some possible factors which can be identified include:

a) Mass transfer resistances at the sample surface increase with sucrose concentration due to viscosity increase. This leads to a reduced effective solids concentration in the solution adjacent to the fruit slice in the non-agitated systems at high solution sucrose concentration. This has two effects in that it reduces the effective ΔC for water that the fruit slice "sees" so the rate of water removal decreases. In addition, the reduction of solids content adjacent to the slice surface for non-agitated systems will also tend to result in reduced solute uptake. Since the MTF values are calculated on the basis of normalized % total solids, a reduction of solids uptake for non-agitated systems will reduce the MTF as a function of sucrose solution concentration. When the solids uptake values are investigated (Tables 1 and 8) it is noted that the differences in solids uptake parallel the relative mass transport coefficient values.

b) The assumption that at the higher solution concentations that the activity differences giving the driving force for mass transport are well modelled by the concentrations may not be valid. It could well be that the relative deviation of Δactivity with respect to Δconcentration increases with concentration. Water activity measurements are being conducted to investigate the validity of this hypothesis. This, in itself, would not account for the differences of agitated and non-agitated systems.

Since, at this time, the calculated mass transport coefficients in agitated systems are not independent of concentration, further discussion for all systems will be in terms of the mass transport factors.

The loss of water from the fruit slices was also evaluated by use of equation 1. In this case, C is the water concentration in the fruit slice at time = t, C_o is the initial water concentration in the fruit slice and C_∞ is the water concentration in the osmosis solution. As noted above, C_∞ does not remain constant due to water loss from the fruit slice and due to solute uptake by the fruit slice. The analysis is also compromised due to the "pseudo-step change" in C at short time due to the rapid absorption (presumably on the surface) of solute. This can result in a complicated diffusion mechanism, since,in the simplist case, the apple interior is at one osmotic potential, the fruit surface layer is apparently at a second osmotic potential and the osmosis solution is at a third potential. Despite these complications, equation 1 gives reasonable relationships for water-loss mass transport factors.

Figure 5 shows the data for 3 osmosis solutions having 60% total solids. Examination of the data points shows the sharp drop in water concentration values which is due to solute uptake. Nevertheless, the regression lines used to obtain the mass transport factor give reasonable correlation coefficients, especially considering that all the data points were used. The slopes (i.e., mass transport factors) for a number of test systems are given in Table 4.

Based on the results of these tests of the applicability of the Fickian diffusion equations, it was decided to analyze the body of data in Table 1 using equation 2 with normalized total solids as the concentration term, (i.e. according to the format of Figure 4). Normalized apple slice solids content are given in Table 5. The rate of increase of the normalized solids content was calculated by fitting a regression line to the normalized solids content-time data points. These dimensionless rates (hr^{-1}) are given in Table 6 with the correlation coefficients for the fit of the line to the data points. In some cases, data points which are greatly removed from the "smooth", solids content-time curve have been omitted. These are marked by an asterisk. The overall mass transport factors which are taken to be the slope of the normalized solids content-$(time)^{1/2}$ line in accordance to equation 2 are given in Table 7, together with the respective correlation coefficients. In further discussion the mass transport factors will be designated by MTF.

The data presented in in Tables 6 and 7 will be discussed below with respect to the influence of various process parameters.

5.3.2 Effect of Solute Concentration

Osmosis with Sucrose has been evaluated at four concentrations. The osmosis rates and mass transport factors are given in Tables 6 and 7 for systems which are agitated or osmosed without agitation. MTF values are also shown in Figure 6. It can be seen that as the sucrose concentration is increased, the rate of osmosis and the MTF values increase. Similar results were found for maltodextrin samples at 25 and 40% solids, and the mixed lactose: sucrose and maltodextrin: sucrose solutions.

5.3.3 Effect of Agitation During Osmosis

Tables 6 and 7 and Figure 6 show that gentle agitation as used in this study has essentially no effect on osmosis rate or MTF at low or medium osmosis solute concentration. As higher solution concentration, there is an increase in osmosis rate and MTF for agitated systems as compared to the non-agitated. As noted earlier, this is undoubtedly due to an increased viscosity of the solution with increasing concentration which results in an increase of the mass transfer resistance in the solution adjacent to the surface of the sample. For non-agitated systems this will result in lower average effective solution concentrations adjacent to the sample surface which gives reduced rates of water loss and lower solute uptake (see section 5.3.4). Agitation of the high viscosity

osmosis solutions results in renewal with fresh solution of the region adjacent to the fruit slice, given higher average solids concentrations.

5.3.4 Solute Uptake Behavior

During the course of osmosis, the apple slices pick up solute. From Table 1, it can be seen that the solids are gained very early in the process and then increase only very slowly during the remainder of the process. No attempt has been made at this time to measure the spatial distribution of the solute. It is likely to be either located in a very thin surface layer, or perhaps in intercellular spaces of the fruit slice which contained air.

Table 8 shows the net solute uptake at the latter stages of the osmosis process. It can be seen that for the sucrose solutions, the solute uptake increases as the concentration increases. As noted above, samples prepared with agitation have higher levels of uptake. This is true for all the solute systems studied. Examination of the results in Table 8 indicates that the uptake values for mixed solutes for solutions of the same total solids content reflect to some extent the uptake values of the individual components at the concentrations present in the mixed solution. The fact that many of the solutes have similar uptake values means that the values for solutions of equal total solids content are similar; salt is a notable exception.

5.4 Effect of Solutes

5.4.1 Lactose as an Osmosis Solute

The disaccharide, sucrose, had been successfully used as an osmosis solute. It was therefore decided to investigate the disaccharide, lactose, for its suitability. Lactose has a much lower level of sweetness than sucrose. It also will be available in increasing quantities as cheese wheys are recovered and fractionated to recover proteins, leaving a lactose rich fraction. One potential problem which required evaluation is the low solubility of lactose in aqueous solution.

5.4.1.1 Pure lactose solutions

The solubility limit for lactose is generally reported to be about 17-20 grams of lactose per 100 grams of solution. In this study lactose solutions were prepared at concentrations of 25-28% by first heating the solution to dissolve the solids and then allowing the solution to cool to room temperature before use. This undoubtedly resulted in a supersaturated solution, though in all the studies conducted with pure lactose solutions, no nucleation of crystals was observed. In a lactose (25%); Sucrose (35%) mixed systems which will be mentioned later, on one occasion, very small lactose crystals were observed to form after a period of standing.

Osmotic preconcentrations of peach slices and banana slices were attempted using lactose solutions at 20 and 28% solids, while a solution at 25% solids was used with apple slices. The osmotic

preconcentration effect was slight for the peach and apple slices. The higher natural solids content of the banana slices made them particularly unsuited for the osmotic preconcentration step with the concentrations which can be attained with lactose solutions. (As an aside, it can be speculated that the high initial solids content is an important factor for the high flavor quality obtained with non-pretreated freeze dried banana). Pure lactose in solution was not particularly promising as an osmosis solute. Tests were conducted on using lactose in the dry state, and in solution in combination with sucrose.

5.4.1.2 Dry lactose and lactose/sucrose mixtures

Fruit slices were mixed with an equal weight of dry lactose powder, and held for 23 hours with periodic shaking. Dry sucrose powder was used for a comparison. The results showed that the lactose powder was only slightly more effective than the saturated lactose solution. Sucrose powder was very effective in removing water, with the sucrose ending up as a sub-saturated solution. It was noted that with the dry lactose, in the initial stages of osmosis the sample loses water to the adjacent layer of lactose which then proceeds to cake and form a shell of low water permeability on the fruit slice. It appears that this shell prevents further transport of water from the fruit slice.

Further studies were conducted to determine if the difficulties associated with the use of lactose could be reduced or eliminated by mixing sucrose with the lactose. Apple slices were

mixed with an equal weight of lactose:sucrose mixtures of varying proportions. The samples were agitated periodically over the 23 hour holding period. The apples were rinsed quickly (2-3 seconds) prior to determining the water loss and solids uptake during the osmosis process. The results show (Figure 7) that while there is a decrease in water removal as lactose replaces sucrose (at constant total amount solids), the mixture act synergistically. The solids content for the fruit slices which Phase II and III studies have shown to be desirable for attaining improved freeze dried quality can be achieved with a day 50:50 mixture of lactose and sucrose. The presence of the sucrose apparently gives flow paths for water removal from the fruit piece so that all the lactose is available as a moisture sink.

It should be noted that apple slices osmotically preconcentrated by placing in dry sucrose increased from 11% to 36% solids. The loss of water was so great with pure dry sucrose that the slices were highly shrunken, giving a poor appearance. This is in contrast to the good slice appearance which is obtained when the osmotic pretreatment is achieved using a 60% sucrose solution. Three hours in a 60% sucrose solution gives apple slices of approximately 30% solids. With the mixed dry solids systems, all samples had reasonably good appearance, being only slightly shrunken.

5.4.1.3 Mixed Lactose:Sucrose Solutions

With the success of the mixed dry sugar systems, tests were conducted to evaluate the potential for mixed lactose:sucrose liquid osmosis systems. Kinetic studies were conducted to determine the effects of different compositions and concentrations on the rate of osmosis of apple slices. The mass transport data are given in Table 1. The osmosis rates and MTF for the lactose:sucrose mixtures are given in Tables 6 and 7. It can be seen that the MTF values increase with increase in total solids from 40 or 50% to 60%. The osmosis rates and MTF values do not appear to depend on agitation.

As was noted above in Section 5.4.1.1, lactose solution near or slightly above its solubility limit is not very effective as an osmotic agent. However, in combinations with sucrose at total concentrations of 40, 50 or 60%, it gives sizable increases in solids content of the apple slices, which are larger than the

sum of the increases which would result from each component at the concentration which is present in the mixture.

5.4.2 Salt as an Osmosis Solute

Sodium chloride has been tested alone at a 25% level and in combination with sucrose at a total concentration of 50% solids (15% salt/35% sucrose). The results given in Tables 6 and 7 show that both osmosis solutions are very effective for concentrating apple slices. The extent to which NaCl can be used as a substitute for sucrose is probably limited due to its salty flavor. Organoleptic evaluations of products obtained from mixed salt-sucrose osmosis treatments are being conducted.

5.4.3 Maltodextrin as an Osmosis Solute

Maltodextrin (DE=15) was evaluated as an osmosis solute, alone at concentrations of 25 and 40% and in combination with sucrose at total solids concentrations of 50% (25% Maltodextrin/25% Sucrose) and 60% (25% maltodextrin/35% sucrose). The measured osmosis rates and MTF are given in Tables 6 and 7, respectively. It can be seen that maltodextrin can be used as an osmosis solute at higher total solids concentration. The 25% maltodextrin is relatively ineffective.

5.5 Effect of Osmosis Solution Total Solids Content for Pure and Mixed Solutes

The measured values of osmosis rates and mass transfer factors which are given in Tables 6 and 7 are presented in Tables 9

and 10 in grouping by total solids.

At the 25% total solids level, salt is by far the best osmosis solute. This is undoubtedly due to its higher molar concentration for a 25% weight concentration and since it ionizes to form two ionic units in solution. The sucrose, lactose and maltodextrin have similar MTF values. At 40% solids, all the solutes tested have similar mass transport factors. Carbohydrate solutions at 50% total solids have similar values of osmosis rate and MTF, the sucrose having a slight advantage. There is little difference between the lactose:sucrose and maltodextrin:sucrose mixtures. The mixed salt:sucrose system shows a very high osmosis rate and MTF value. Again this is probably due to the ionization of the salt and the high mole fraction relative to the weight percentage. However, this cannot be the entire explanation since on this basis the 25% NaCl solution which has a higher mole fraction of ionized species should have a higher osmosis rate than the mixed sucrose:salt system.

The osmotic solutions at 60% solids are effective, though the rate with sucrose (with agitation) is somewhat higher than the two mixed systems. The mixed systems at 60% solids are as effective as pure sucrose at 50% solids. With the unagitated systems, the three solute systems have similar MTF values.

The results show that mixed solute systems can be effective for preconcentrating fruit slices prior to freeze drying. The choice of solute systems can thus be made on the basis of organoleptic and economic factors.

Table 1: Mass Transport data during Osmotic Preconcentration of Apple Slices

	time (with agitation)						time (without agitation)					
	0	1/2	1	2	3	4	0	1/2	1	2	3	4
25% Sucrose												
SG[a]	0	1.2	2.0	2.4	2.2	3.6	0	4.7	4.1	3.4	4.6	4.1
WL	0	-3.0	-2.7	0.3	2.7	3.6	0	-0.2	-0.3	3.2	7.0	4.7
TS	14.2	14.7	13.5	16.2	16.8	17.8	12.1	16.0	15.5	15.5	17.2	16.3
25% Sucrose (#2)												
SG							0	2.9	4.1	3.8	4.5	6.1
WL							0	-2.3	-1.8	1.5	2.5	4.4
TS							12.2	14.4	15.4	15.6	16.4	18.1
40% Sucrose												
SG	0	3.4	7.2	5.0	8.9	4.5	0	5.5	5.4	6.5	8.9	7.3
WL	0	1.1	4.3	9.8	20.6	21.3	0	6.1	8.1	12.3	17.0	20.8
TS	14.9	18.1	21.4	20.9	27.1	23.3	13.6	19.2	19.6	21.3	24.4	24.2
40% Sucrose (#2)												
SG							0	8.1	7.4	9.0	9.7	9.2
WL							0	0.9	3.3	8.4	11.0	15.0
TS							14.1	20.7	20.6	23.0	24.0	24.6
50% Sucrose												
SG	0	10.9	10.1	13.9	14.4	10.9	0	12.8	7.3	10.8	10.7	10.3
WL	0	6.5	12.9	20.9	48.7	32.8	0	5.4	13.4	15.3	22.4	26.3
TS	12.0	21.9	22.6	27.8	40.0	29.2	11.8	22.9	20.4	23.7	25.6	26.3
50% Sucrose (#2)							0	8.8	9.0	10.7	10.2	13.0
SG							0	3.3	7.9	15.1	16.5	26.6
WL							14.7	22.3	23.3	26.5	26.6	32.1
TS												

Table 1 (continued)

	time (with agitation)						time (without agitation)					
	0	1/2	1	2	3	4	0	1/2	1	2	3	4
60% Sucrose												
SG	0	13.5	17.8	16.5	16.7	22.0	0	10.3	13.[illegible]	13.7	12.1	10.6
WL	0	8.5	20.4	35.4	57.0	42.5	0	7.8	11.2	18.9	24.4	27.7
TS	11.8	24.1	30.4	34.8	48.0	42.5	11.5	21.3	24.2	26.7	26.8	26.8
60% Sucrose (#2)							0	12.8	12.4	14.4	14.0	15.2
							0	9.8	14.5	23.8	27.2	30.2
							12.6	24.7	25.5	29.9	30.7	32.7
25% Lactose												
SG	0	4.7	3.4	5.9	5.1	6.2	0	1.5	1.8	1.6	1.7	2.7
WL	0	-2.8	-0.9	-0.5	2.4	1.5	0	-0.2	-0.3	3.2	7.0	4.7
TS	12.4	15.8	15.2	17.2	17.0	17.9	14.1	14.9	15.2	15.4	15.2	16.6
25% Lactose 15% Sucrose												
SG	0	6.2	6.5	9.7	3.6	11.6	0	7.1	6.8	7.5	8.4	9.6
WL	0	1.7	4.8	10.1	5.9	19.9	0	0.9	4.4	8.7	10.7	14.2
TS	14.5	19.8	20.6	24.2	18.7	28.5	11.6	17.6	18.0	19.3	20.5	22.3
25% Lactose 25% Sucrose												
SG	0	11.7	9.3	8.3	10.4	10.1	0	5.7	5.7	8.3	7.7	8.3
WL	0	5.7	8.6	13.3	15.0	24.7	0	3.1	3.5	10.1	10.0	16.8
TS	14.0	24.2	23.1	23.5	25.6	28.2	11.5	16.8	16.8	20.1	19.9	21.7
25% Lactose 35% Sucrose												
SG	0	11.2	11.8	11.6	13.5	13.1	0	12.4	11.8	9.6	9.0	13.7
WL	0	10.1	14.7	22.8	36.7	35.6	0	14.7	20.5	22.6	29.7	38.3
TS	13.1	23.9	25.7	27.8	34.5	33.8	10.7	23.7	24.7	23.2	24.8	32.3

Table 1 (continued)

	time (with agitation)						time (without agitation)					
	0	1/2	1	2	3	4	0	1/2	1	2	3	4
25% NaCl												
SG	0	9.2	10.1	10.9	13.0	14.0	0	7.1	7.3	8.1	9.3	11.2
WL	0	15.5	22.7	28.3	33.8	33.5	0	8.5	14.7	22.9	25.9	27.5
TS	13.5	24.2	27.1	29.6	33.5	34.1	12.9	20.3	21.8	24.6	26.7	28.8
15% NaCl 35% Sucrose												
SG	0	11.1	15.4	16.7	14.9	14.8	0	7.8	8.2	12.3	10.8	12.3
WL	0	22.4	30.5	43.6	45.6	53.0	0	16.8	24.4	41.7	41.2	49.9
TS	10.9	24.8	31.2	37.8	37.3	41.7	13.2	23.1	25.5	36.1	34.5	41.0
25% Maltodextrin												
SG	0	4.9	4.4	5.3	5.4	5.1						
WL	0	-7.7	-8.8	-10.0	-7.0	0						
TS	12.9	15.8	15.3	15.7	16.3	17.2						
40% Maltodextrin												
SG	0	7.7	7.7	9.8	9.5	6.2						
WL	0	-4.6	-3.5	-3.1	0.3	5.7						
TS	13.0	18.5	18.6	20.1	20.6	19.2						
25% Maltodextrin 25% Sucrose												
SG	0	14.5	10.2	11.7	9.8	10.2						
WL	0	1.1	10.2	17.1	26.1	34.5						
TS	15.3	26.3	25.6	28.4	29.9	33.3						

Table 1 (continued)

	time (with agitation)						time (without agitation)					
	0	1/2	1	2	3	4	0	1/2	1	2	3	4
25% Maltodextrin 35% Sucrose												
SG	0	12.6	12.0	15.1	14.0	10.9	0	10.7	11.6	13.0	9.4	9.1
WL	0	16.8	14.8	22.3	31.9	34.3	0	4.1	7.2	17.9	18.0	24.3
TS	11.5	25.3	24.2	28.6	31.0	29.3	12.0	21.4	22.6	26.2	23.4	24.9
H_2O												
SG	0	-2.6	-4.2	-5.3	-6.7	-7.8						
WL	0	-24.9	-26.9	-31.3	-24.8	-39.1						
TS	14.4	9.6	8.4	7.4	6.4	5.0						

a) SG = Solids gained (grams of solids gained per 100 grams of initial apple weight)

WL = Water lost (grams of water lost per 100 grams of initial apple weight)

TS = Total solids (actual percentage of solids at time reflecting initial solids content, solids gained and water lost)

Table 2

Mass transport factors as measured by slopes of C vs. $t^{1/2}$ relationships in Figures 1-4. (Relative rates in parentheses)

Concentration Basis

	$gH_2O/100g$ apples	$\frac{g\ H_2O\ loss}{g\ H_2O\ initial}$	% total solids	$\frac{(\%\ total\ solids)t}{(\%\ total\ solids)_o}$
25% Sucrose	3.8 (0.32)	0.02 (0.14)	1.9 (0.37)	0.12 (0.35)
40% Sucrose	12.0 (1.00)	0.14 (1.00)	5.2 (1.00)	0.34 (1.00)
50% Sucrose	21.7 (1.81)	0.25 (1.79)	11.1 (2.13)	0.73 (2.15)
60% Sucrose	27.4 (2.28)	0.31 (2.21)	17.2 (3.31)	1.33 (3.91)

Table 3

Mass Transport Coefficients (K) as Determined from MTF and C_∞ values

	agitated			non-agitated		
Sucrose Concentration	MTF[a]	C_∞[b]	K	MTF	C_∞	K
25%	0.12	1.3	0.092	0.19	1.4	0.136
40%	0.34	1.6	0.213	0.37	1.8	0.206
50%	0.72	2.5	0.282	0.54	2.3	0.235
60%	1.33	3.5	0.380	0.71	2.5	0.284

a) Mass Transport Factors

b) Normalized % solids content extrapolated to infinite time

Table 4

Mass Transport factors as measured by slopes of $\log\frac{C-C_{\infty}}{C_o-C_{\infty}}$ vs t relationships for osmosis preconcentration of apple slices

Sample	Mass Transport factor	
	with agitation	without agitation
Sucrose 25%	-	0.034
Sucrose 40%	0.052	0.051
Sucrose 50%	-	0.040
Sucrose 60%	0.110	0.034
Lactose 25% Sucrose 35%	0.059	-
Maltodextrin 25% Sucrose 35%	0.042	-

Table 5

Normalized Solids Content[b] for Osmotically Concentrated Apple Slices

Sample[a]	time (with agitation) 0	1/2	1	2	3	4	time (without agitation) 0	1/2	1	2	3	4
25% Sucrose (#1)	1.00	1.04	0.95	1.14	1.18	1.25	1.00	1.18	1.26	1.28	1.34	1.48
25% Sucrose (#2)							1.00	1.32	1.28	1.28	1.42	1.35
40% Sucrose (#1)	1.00	1.21	1.44	1.40	1.82	1.56	1.00	1.47	1.46	1.63	1.70	1.74
40% Sucrose (#2)							1.00	1.41	1.44	1.57	1.79	1.78
50% Sucrose (#1)	1.00	1.83	1.88	2.32	3.33	2.43	1.00	1.52	1.59	1.80	1.81	2.18
50% Sucrose (#2)							1.00	1.94	1.73	2.01	2.17	2.23
60% Sucrose (#1)	1.00	2.80	3.20	3.03	3.90	3.38	1.00	1.96	2.02	2.37	2.44	2.60
60% Sucrose (#2)	1.00	2.04	2.58	2.95	4.07	3.60	1.00	1.85	2.10	2.32	2.33	2.33
25% Lactose	1.00	1.27	1.23	1.39	1.37	1.44	1.00	1.06	1.08	1.09	1.08	1.18
25% Lact/15%Sucr	1.00	1.37	1.42	1.67	1.29	1.97	1.00	1.52	1.55	1.66	1.77	1.92
25% Lact/25%Sucr	1.00	1.73	1.65	1.68	1.83	2.01	1.00	1.46	1.46	1.75	1.73	1.89
25% Lact/35%Sucr	1.00	1.82	1.96	2.12	2.63	2.58	1.00	2.21	2.31	2.17	2.32	3.02
25% NaCl	1.00	1.79	2.01	2.19	2.48	2.53	1.00	1.57	1.69	1.91	2.07	2.23
15% NaCl/35%Sucr	1.00	2.28	2.86	3.47	3.42	3.83	1.00	1.75	1.93	2.73	2.61	3.11
25% Maltodextrin	1.00	1.22	1.19	1.22	1.26	1.33						
40% Maltodextrin	1.00	1.42	1.43	1.55	1.58	1.48						
25% MD/25% Sucr	1.00	1.72	1.67	1.86	1.95	2.18						
25% MD/35% Sucr	1.00	2.20	2.10	2.49	2.70	2.55	1.00	1.78	1.88	2.18	1.95	2.08

a) Sucr = Sucrose
Lact = Lactose
NaCl = Salt
MD = Maltodextrin

b) $\frac{\text{Solids content at time}}{\text{Solids content initially}}$

Table 6

Osmosis Rates Based on
Normalized % Total Solids for
Preconcentration of Apple Slices

Osmosis Solution	Osmosis Rate (hr^{-1}) With Agitation Rate[a]	r[b]	Without Agitation Rate	r
25% Sucrose	0.075	0.91	0.075	0.96
40% Sucrose	0.115	0.73	0.104	0.96
50% Sucrose	0.180	0.91*	0.168	0.96*
60% Sucrose	0.411	0.97*	0.186	0.93*
25% Lactose	0.054	0.89	0.027	0.82
25%Lact/15%Sucr	0.177	0.99*	0.114	0.99
25%Lact/25%Sucr	0.123	0.96*	0.126	0.94
25%Lact/35%Sucr	0.243	0.95	0.230	0.94*
25% NaCl	0.213	0.97	0.188	0.99
15%NaCl/35%Sucr	0.392	0.92	0.373	0.94
25% Maltodextrin	0.034	0.90	-	-
40% Maltodextrin	0.071	0.96*	-	-
25% MD/25%Sucr	0.137	0.97	-	-
25% MD/35%Sucr	0.233	0.94*	0.073	0.96*

a) Osmosis Rate-(change in Normalized % Total Solids per hour)

b) Correlation coefficient- * indicates that a single data point of questionable validity omitted from calculations

Table 7

Mass Transport Factors for Osmotic Preconcentration of Apple Slices Based on Normalized % Total Solids (See Text)

Osmosis Solution	Mass Transport Factor ($hr^{-\frac{1}{2}}$) With Agitation MTF[a]	r[b]	Without Agitation MTF	r
25% Sucrose	0.12	0.98*	0.19	0.91
40% Sucrose	0.34	0.89	0.37	0.97
50% Sucrose	0.72	0.96*	0.54	0.93
60% Sucrose	1.33	0.92	0.71	0.94
25% Lactose	0.21	0.95	0.07	0.89
25%Lact/15%Sucr	0.48	0.99*	0.42	0.97
25%Lact/25%Sucr	0.42	0.90	0.43	0.97
25%Lact/35%Sucr	0.80	0.98	0.79	0.89
25% NaCl	0.76	0.98	0.59	0.99
15% NaCl/35%Sucr	1.39	0.98	1.04	0.98
25% Maltodextrin	0.14	0.92	-	-
40% Maltodextrin	0.33	0.95*	-	-
25% MD /25%Sucr	0.52	0.95	-	-
25% MD /35%Sucr	0.77	0.91	0.50	0.87

a) MTF - Calculated from the slope of Normalized % Total Solids vs $(time)^{\frac{1}{2}}$ curves

b) Correlation coefficient- * indicates that a single data point of questionable validity omitted from calculations

Table 8

Average Gain of Solute by Apple Slices

Following Osmotic Preconcentration

Solution	Average Solute Gain (g solute/ 100 g apple) With agitation	without agitation
25% Sucrose	2.7	4.4
40% Sucrose	6.1	8.4
50% Sucrose	13.1	11.0
60% Sucrose	18.4	13.3
25% Lactose	5.7	2.0
25%Lact/15%Sucr	10.6	8.5
25%Lact/25%Sucr	9.6	8.1
25%Lact/35%Sucr	12.7	10.8
25% NaCl	12.6	9.5
15%NaCl/35%Sucr	15.5	11.8
25% Maltodextrin	5.3	-
40% Maltodextrin	8.5	-
25% MD/25% Sucr	10.6	-
25% MD/35% Sucr	13.3	10.5
Water	-6.6	-

Table 9

Rate of Increase of Normalized % Total Solids for Osmotic Preconcentration of Apple Slices

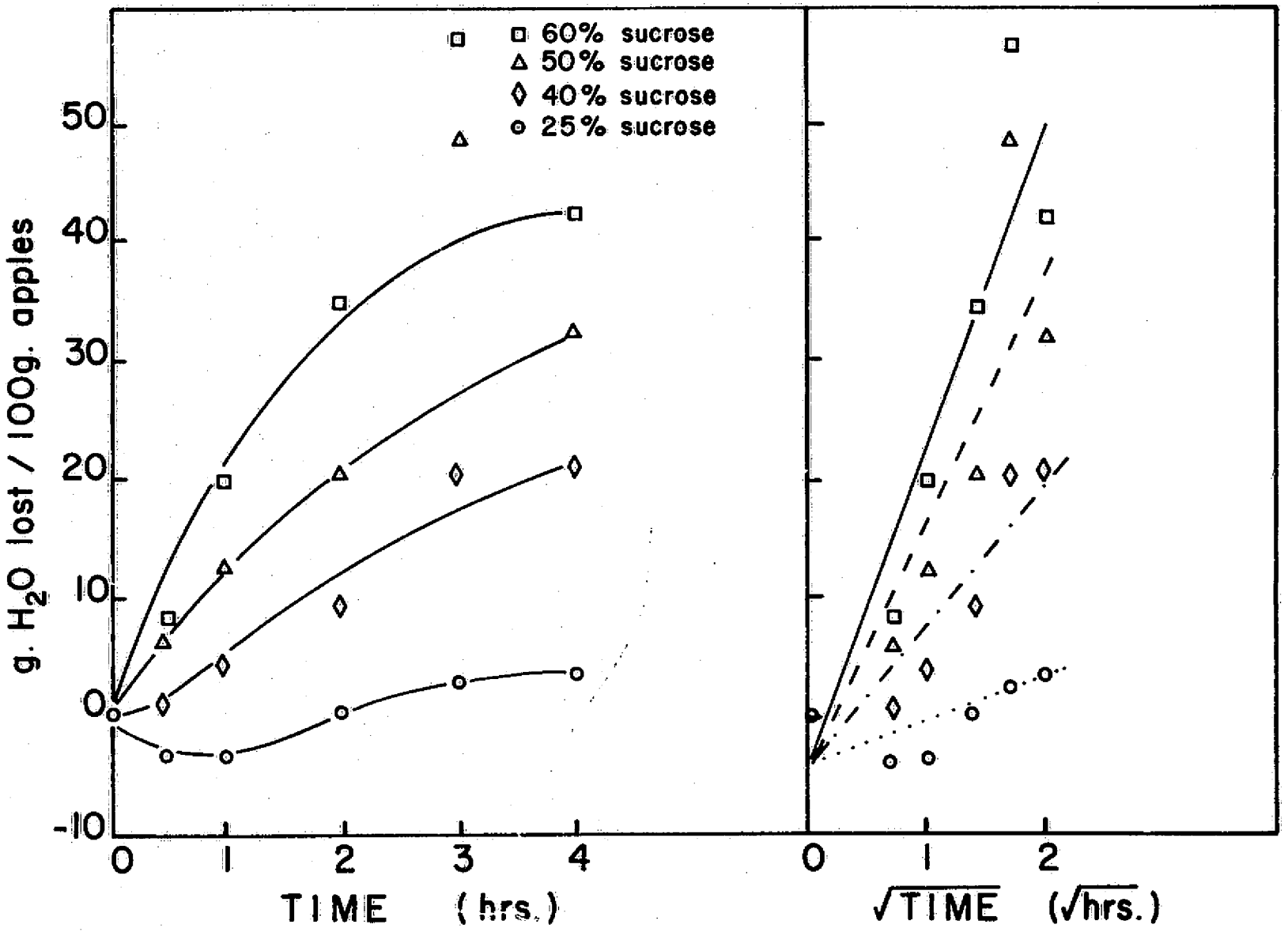
Osmosis Solution	Osmosis Rate (hr^{-1}) With Agitation	Without Agitation
25% Solids		
Sucrose	0.075	0.075
Lactose	0.054	0.027
Maltodextrin	0.034	-
NaCl	0.213	0.188
40% Solids		
Sucrose	0.115	0.104
25% Lact/15% Sucr	0.177	0.114
Maltodextrin	0.071	-
50% Solids		
Sucrose	0.180	0.168
25%Lact/25%Sucr	0.123	0.126
15%NaCl/35%Sucr	0.392	0.373
25% MD /25%Sucr	0.137	-
60% Solids		
Sucrose	0.411	0.186
25%Lact/35%Sucr	0.243	0.230
25% MD /35%Sucr	0.233	0.073

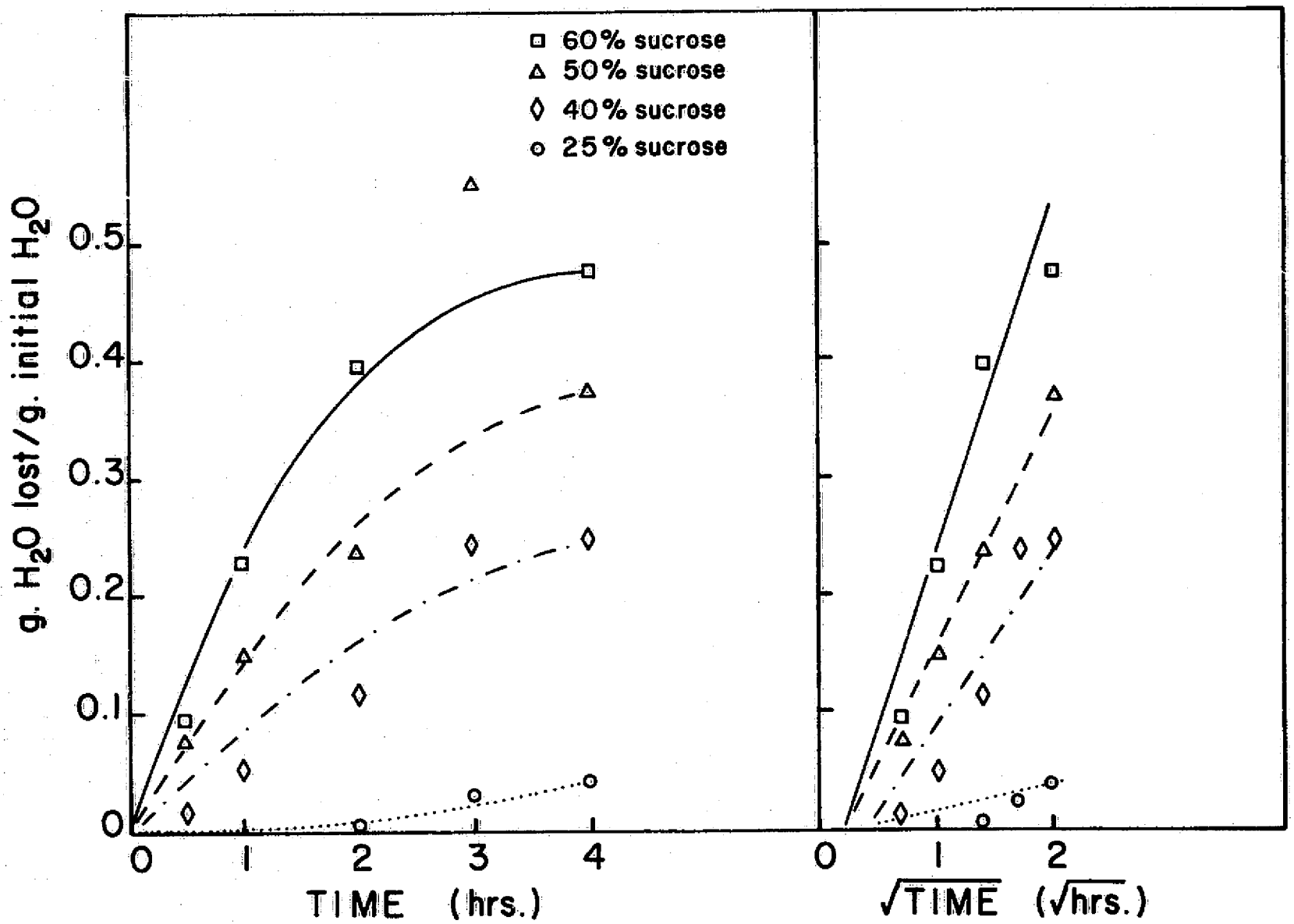
Table 10

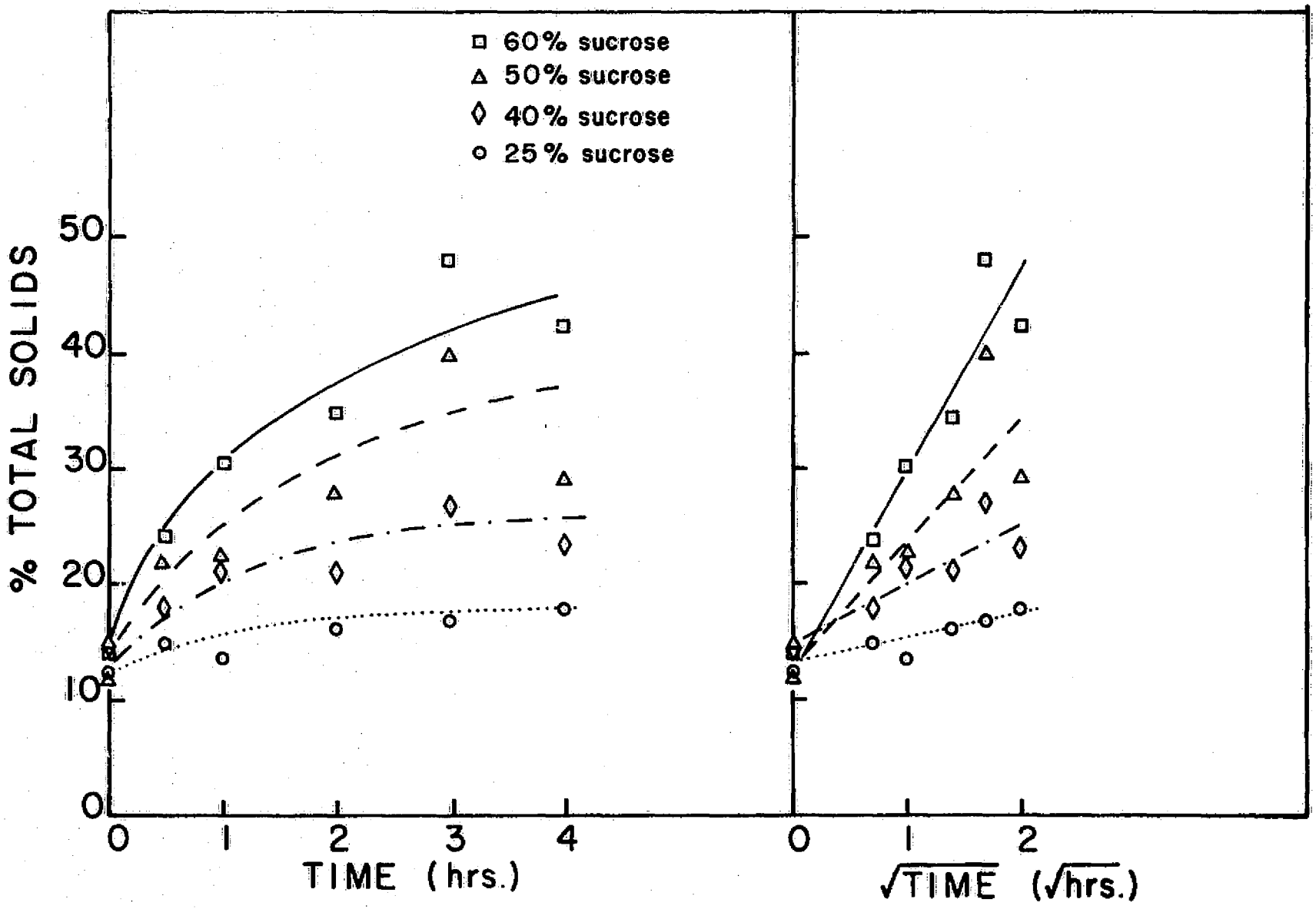
Mass Transport Factors for
Osmotic Preconcentration of Apple Slices

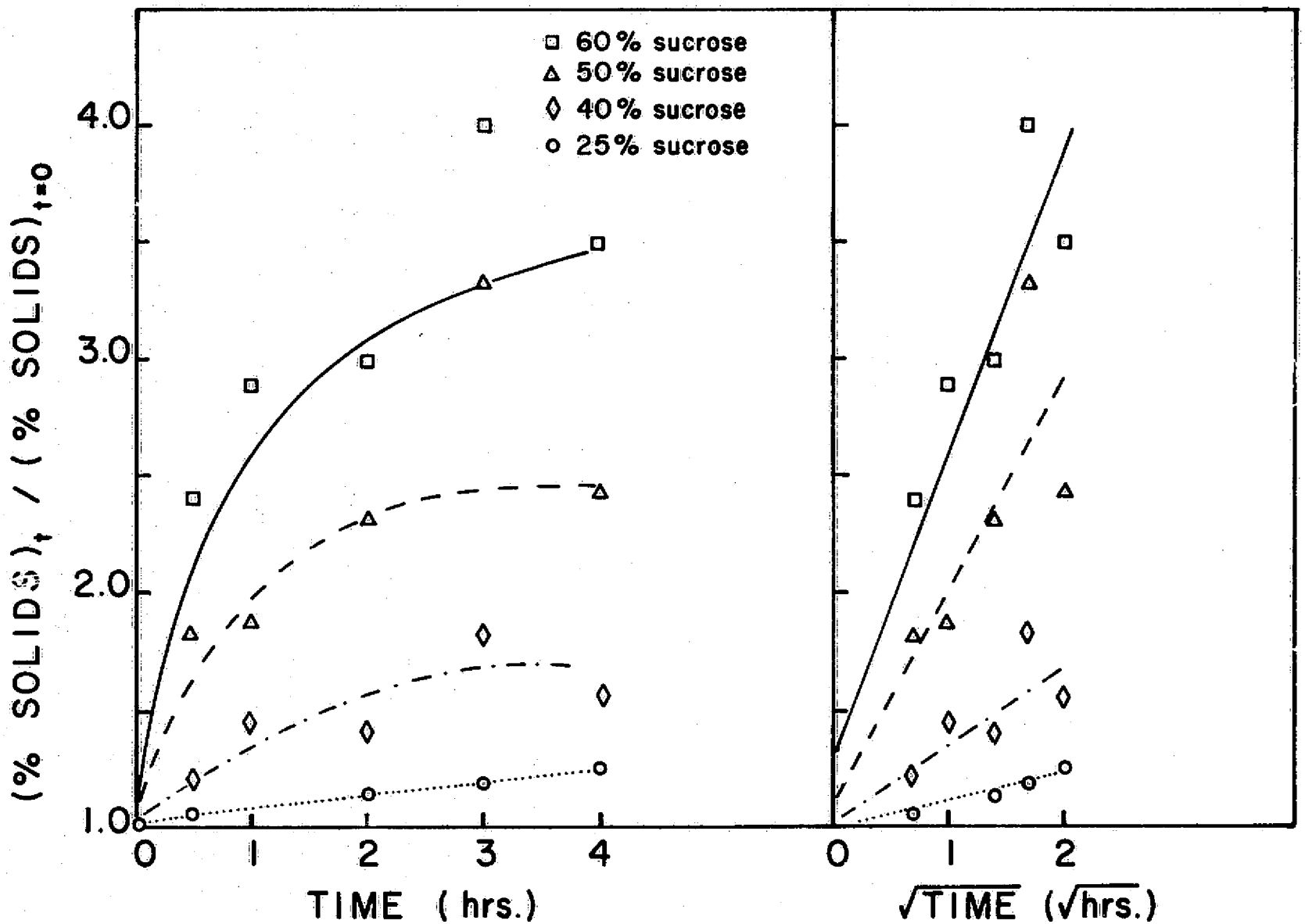
Osmosis Solution	Mass Transport Factor ($hr^{-1/2}$) With Agitation	Without Agitation
25% Solids		
Sucrose	0.12	0.19
Lactose	0.21	0.07
Maltodextrin	0.14	-
NaCl	0.76	0.59
40% Solids		
Sucrose	0.34	0.37
25%Lact/15%Sucr	0.48	0.42
Maltodextrin	0.33	-
50% Solids		
Sucrose	0.72	0.54
25%Lact/25%Sucr	0.42	0.43
15%NaCl/35%Sucr	1.39	1.04
25% MD /25%Sucr	0.52	-
60% Solids		
Sucrose	1.33	0.71
25%Lact/35%Sucr	0.80	0.79
25% MD /35%Sucr	0.77	0.50

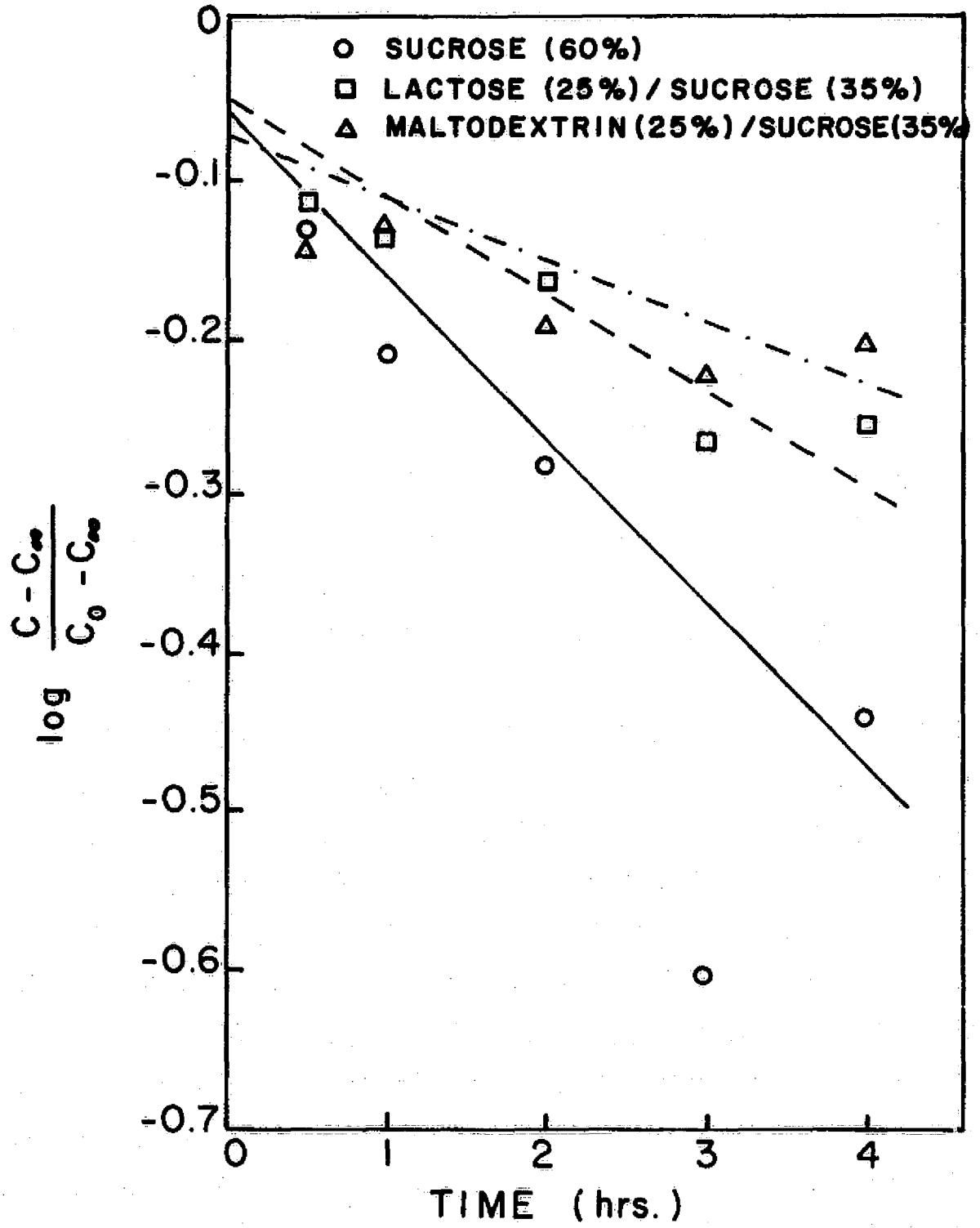
List of Figures

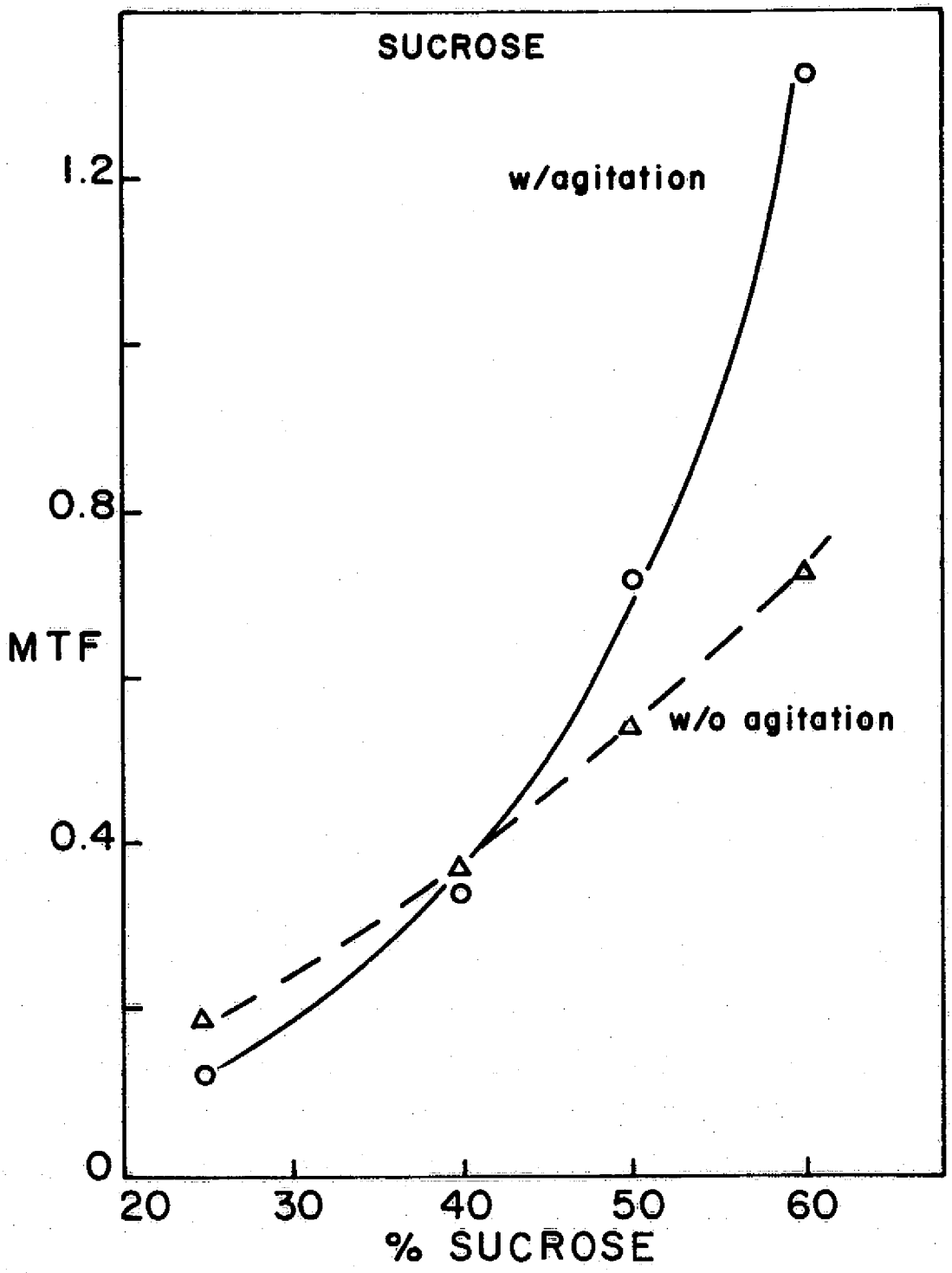

60% sucrose
50% sucrose
40% sucrose
25% sucrose
g. H_2O lost / 100g. apples
50
40
30
20
10
0
-10
0
1
2
3
4
TIME (hrs.)
0
1
2
√TIME (√hrs.)

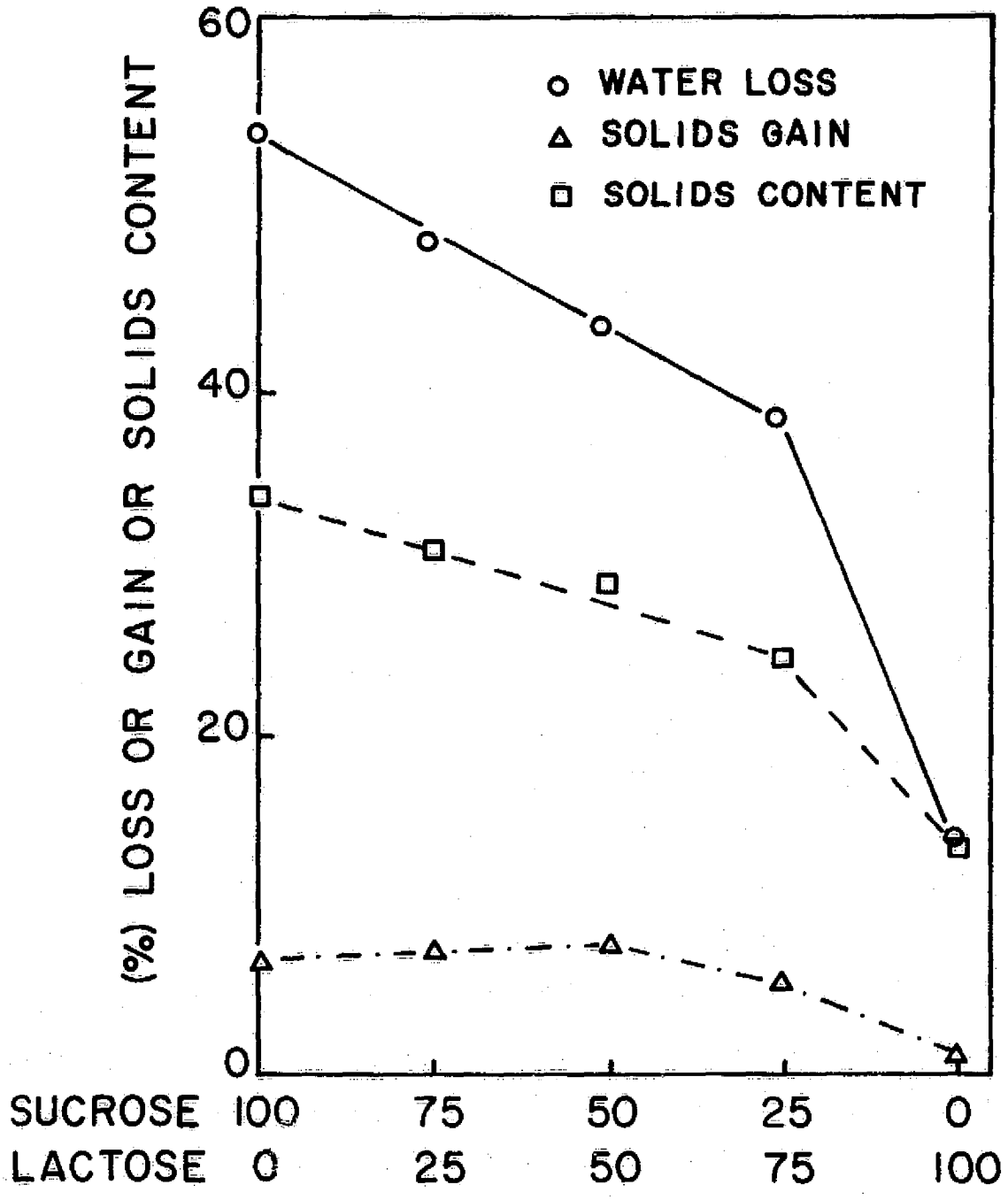

60% sucrose
50% sucrose
40% sucrose
25% sucrose
g. H2O lost/g. initial H2O
0.5
0.4
0.3
0.2
0.1
0
0
1
2
3
4
TIME (hrs.)
0
1
2
√TIME (√hrs.)


60% sucrose
50% sucrose
40% sucrose
25% sucrose
% TOTAL SOLIDS
0
10
20
30
40
50
0
1
2
3
4
TIME (hrs.)
0
1
2
√TIME (√hrs.)


60% sucrose
50% sucrose
40% sucrose
25% sucrose
(% SOLIDS)t / (% SOLIDS)t=0
4.0
3.0
2.0
1.0
0
1
2
3
4
TIME (hrs.)
0
1
2
√TIME (√hrs.)


SUCROSE (60%)
LACTOSE (25%) / SUCROSE (35%)
MALTODEXTRIN (25%) / SUCROSE (35%)
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
0
1
2
3
4
TIME (hrs.)
log (C - C∞) / (C0 - C∞)


SUCROSE
w/agitation
w/o agitation
MTF
1.2
0.8
0.4
0
20
30
40
50
60
% SUCROSE


60
40
20
0
(%) LOSS OR GAIN OR SOLIDS CONTENT
WATER LOSS
SOLIDS GAIN
SOLIDS CONTENT
SUCROSE 100 75 50 25 0
LACTOSE 0 25 50 75 100

6. Storage Stability of Osmotically Preconcentrated Freeze Dried Fruits

6.1 Introduction

Studies on the storage stability of freeze dried osmotically pretreated fruit slices has continued during Phase IV. One study, with freeze dried peaches, was completed during Phase III, and the results presented and discussed in the Phase III Annual Report. At the end of Phase III, a longer term storage stability study was initiated with freeze dried apples; this study has passed 1 year and is continuing with one additional organoleptic evaluation scheduled for July 1976 (See program schedule, Table 1). Storage parameters being investigated are package headspace atmosphere (air vs. vacuum), sample water content and storage temperature.

The evaluation of stability of these freeze dried products is necessary to develop information on the temperatures and moisture levels which can be tolerated during storage. This information will be utilized in conjunction with mass transport kinetics of packaging materials to define expected storage life for various packaging configurations and storage conditions.

6.2 Methods

The freeze dried apple slices used in the storage stability study were prepared according to the following procedures:

6.2.1 Sample Preparation

Ninety (90) lbs. of fresh apples were manually peeled and sliced. The sliced apples were osmotically concentrated by placing them in a circulating carbohydrate solution for about 3-4 hours. The solutions used were either 60% sucrose or 45% maltodextrin (DE=15). Both solutions contained 0.52% ascorbic acid and 0.14% malic acid to prevent browning during handling. The concentrated apples are rinsed for about 20 seconds in cold water containing 0.52% ascorbic acid to remove surface carbohydrate, spread in thin layers on trays, frozen at -25°C and freeze dried.

6.2.2 Packaging and Storage Tests

Following freeze drying the apple slices were exposed to relative humidities of 0% (drierite), 10% (Z_nCl_2) and 43% (K_2CO_3). The moisture equilibration of the apples at the different water activities took about 12 days. For the first six days, the apple slices were left to equilibrate in closed desiccators under air. Due to the slow rate of equilibration observed, for the remaining time, the apples were equilibrated under vacuum.

The equilibrated samples were sealed into cans. Samples at the three relative humidities were sealed with air in the headspace. Samples at 0%RH were prepared with an evacuated headspace. The sealed containers were stored at 4°C, 22°C (room temperature) and 37°C. Zero time for the storage test was taken to be the time

that the apples were removed from the desiccators to be sealed in the containers. The complete listing of sample and storage conditions, and sampling intervals, is given in Table 1.

6.2.3 Organoleptic Evaluation Procedure

Two types of organoleptic evaluation were used to determine the effects of process variables on product quality. The samples were evaluated both as dry and rehydrated product. Rehydrated samples are first ground to a powder in blender and then rehydrated to 65% water content to eliminate the effect of texture on the organoleptic evaluation. Products were evaluated by difference tests for taste and texture on a nine point hedonic scale (9= "like extremely", 1= "dislike extremely"), and by a ranking test where samples are rated in order of preference. The test forms are shown in Figures 2 and 3. By analysis of variance, the difference between samples can be evaluated for significance. In addition, the average value of the hedonic rating scores can be used as a measure of product acceptability. The organoleptic testing procedures are more fully described in Larmond (Methods for Sensory Evaluation of Foods, Publication 1284, Canadian Dept. of Agriculture).

6.3 Results of Storage Stability Tests

The moisture uptake by the freeze dried apple slices is shown in Figure 1. If it is assumed that the sample held over drierite is essentially at 0% water, the equilibrium values in

Figure 1 can be used to calculate the moisture contents of the apple slices. The apples coming directly from the freeze dryer have a moisture content of 1 g/100g solids and an Aw of about 0.10. The samples equilibrated at 43%RH have an equilibrium moisture content of 8 g/100g solids.

Tabulated data for the taste and texture scores for the dry and rehydrated products are given in Tables 2 and 3 and the ranking evaluations are presented in Tables 4 and 5. Typical examples of statistical significance of the data in Tables 2-5 are given in Tables 6-9. The amount of information contained in Tables 4 and 5 makes analysis of particular points inconvenient and thus the influence of various parameters have been presented in Figures 4-6.

Figure 4 shows that little difference exists between 0%RH samples which were vacuum sealed or sealed in air and stored at 22°C. Both remained highly acceptable for 52 weeks of storage, indicating that the presence of oxygen at low water activity has little effect on storage stability of apple slices. This contrasts with the Phase III Annual Report in which the presence of oxygen did have a slight effect on the organoleptic quality of the stored peach slices. It seems likely that this is due to differences in the constituents which comprise the respective fruit essences.

Figure 5 shows the effect of sample moisture content on the organoleptic quality of apple slices stored at 22°C. Sucrose-treated apple slices at 0%RH stored either in air or vacuum have high average scores through 52 weeks (1 year) of storage. Samples at 10% RH were not rated significantly different through 8 weeks

of storage, though towards the end the scores are showing a decrease. At 43%RH the taste and texture were much lower, the products being rated unacceptable after only two weeks.

Storage tests were conducted on dry samples at three temperatures (Figure 6). No significant difference was noted between samples stored at 4 and 22°C. Storage at 37°C did result in lowered acceptability scores, though they were not statistically significantly lower than samples stored at 4 or 22°C.

Similar behavior to that noted above for sucrose-pretreated samples was found throughout the 16 week storage period for apple slices preconcentrated with maltodextrin solutions. In general, the average scores of the maltodextrin treated apples are slightly lower than the sucrose treated apples. This had also been noted with peach slices.

With both osmotic pretreatments, the flavor scores were generally higher than the texture scores. The flavor scores for the rehydrated samples were generally higher than the corresponding scores for the dry product. Scores for rehydrated maltodextrin treated apples were lower than for the rehydrated sucrose treated apples.

At storage periods of 6 and 8 months, a commercial applesauce product was included for organoleptic evaluation with the rehydrated ground apple samples. On both occasions the commercial applesauce received lower scores than the rehydrated ground apple slices, indicating that the freeze dried products were highly acceptable after long term storage.

The results of this long term storage test indicates that the osmotically preconcentrated freeze dried apple slices are a well accepted product for both flavor and texture in both the dry and rehydrated state. The sucrose treated slices were again rated above the maltodextrin. As had been shown in the Phase III storage test with peach slices, the major cause of organoleptic quality deterioration is moisture uptake. Temperature of storage above ambient has only a slight effect on quality. The combination of elevated temperature and moisture yielded what was obviously the poorest product.

Table 1

Program for Evaluation of Storage Stability of Osmotically Pretreated Freeze Dried Apples

Sample	0	2wk	5wk	8wk	16wk	6mo	8mo	12mo	18mo
Aw=0[a]									
4°C		S/M[c]	S/M	S/M			S		S
22°C	S/M	S	S/M	S	S/M	S	S	S	S
37°C			S/M	S	S/M				
22°C(V)[b]			S/M	S/M	S/M	S	S	S	S
Aw=0.10									
22°C	S/M	S/M	S/M	S/M					
37°C		S/M	S/M						
Aw=0.43									
22°C	S/M	S/M	S/M	S/M					
37°C		S/M	S/M						

a) Aw = Water activity

b) V = Vacuum sealed

c) S = Sucrose preconcentration

M = Maltodextrin preconcentration

Table 2

Hedonic Tests Scores for Organoleptic Difference Test for Stored Sucrose Preconcentrated Freeze Dried Apple Slices

Time	22/0/V[a]	4/0	22/0	37/0	22/10	37/10	22/43	37/43
				TEXTURE (DRY)				
0 wk	-	-	6.75	-	6.75	-	3.67	-
2 wk	-	7.31	7.15	-	7.15	7.23	3.85	3.62
5 wk	7.08	6.42	7.08	6.83	7.25	6.42	4.67	4.75
8 wk	6.75	7.08	7.00	6.08	6.42	-	4.58	-
16 wk	6.82	-	7.27	6.64	-	-	-	-
6 mo	7.40	-	7.67	-	-	-	-	-
8 mo	7.80	7.70	7.40	-	-	-	-	-
12 mo	7.00	-	7.00	-	-	-	-	-
				TASTE (DRY)				
0 wk	-	-	7.33	-	7.25	-	6.92	-
2 wk	-	7.85	7.31	-	7.38	7.08	5.92	4.62
5 wk	7.25	6.75	7.33	6.50	7.33	6.17	6.42	5.67
8 wk	6.83	7.58	7.08	5.42	6.17	-	5.42	-
16 wk	7.18	-	7.64	6.91	-	-	-	-
6 mo	7.47	-	7.67	-	-	-	-	-
8 mo	7.70	8.10	7.40	-	-	-	-	-
12 mo	7.42	-	7.17	-	-	-	-	-
				TASTE (REHYDRATED)				
0 wk	-	-	7.60	-	7.70	-	7.40	-
2 wk	-	7.42	7.33	-	7.00	7.42	5.75	5.83
5 wk	7.40	8.00	7.70	7.30	7.10	6.60	7.00	5.20
8 wk	7.67	7.17	7.75	6.33	6.92	-	5.08	-
16 wk	7.00	-	7.58	6.50	-	-	-	-
6 mo	[b]8.31	-	7.92	-	-	-	-	-
8 mo	[c]7.45	7.72	7.36	-	-	-	-	-
12 mo	7.75	-	7.67	-	-	-	-	-

[a] Storage Conditions: Temperature (°C) / Relative Humidity (%)
V = Vacuum sealed; all other samples sealed in air

[b] Commercial applesauce = 7.62

[c] Commercial applesauce = 6.18

Table 3

Hedonic Test Scores for Organoleptic Difference Test for Maltodextrin Preconcentrated Freeze Dried Apple Slices

Time	22/0/V[a]	4/0	22/0	37/0	22/10	37/10	22/43	37/43
				TEXTURE (DRY)				
0 wk	-	-	6.00	-	6.46	-	3.92	-
2 wk	-	6.50	-	-	6.17	6.58	3.33	3.50
5 wk	6.31	6.54	6.69	5.85	5.38	6.15	3.83	2.62
8 wk	7.08	6.92	-	-	6.58	-	4.08	-
16 wk	6.85	-	5.77	5.77	-	-	-	-
				TASTE (DRY)				
0 wk	-	-	6.00	-	7.08	-	5.00	-
2 wk	-	6.83	-	-	5.83	6.17	4.58	4.58
5 wk	5.77	6.08	5.85	5.46	5.77	5.62	4.08	3.00
8 wk	6.08	6.83	-	-	6.58	-	4.67	-
16 wk	6.38	-	6.08	5.46	-	-	-	-
				TASTE (REHYDRATED)				
0 wk	-	-	7.08	-	7.08	-	5.25	-
2 wk	-	7.64	-	-	7.73	6.91	5.18	4.09
5 wk	6.64	6.21	6.79	6.79	6.29	5.71	5.14	2.86
9 wk	6.80	7.20	-	-	6.70	-	5.20	-
16 wk	6.83	-	6.58	5.00	-	-	-	-

a) Storage Conditions: Temperature (°C) / Relative Humidity (%)
V = Vacuum sealed; all other samples sealed in air

Table 4

Ranking Order for Stored Sucrose Preconcentrated Freeze Dried Apple Slices

	1st.	2nd.	3rd.	4th.	5th.	6th.	7th.	8th.
			Evaluated Dry					
wks.								
0	22/0[a]	22/10	22/43					
2	4/0	22/10	37/10	22/0	22/43	37/43		
5	22/0	4/0	22/10	22/vac[b]	37/10	22/43	37/0	37/43
8	4/0	22/0	22/vac	22/10	37/0	22/43		
16	22/0	22/vac	37/0					
mos.								
6	22/0	22/vac						
8	4/0	22/0	22/vac					
12	22/vac.	22/0						
			Evaluated Rehydrated					
wks.								
0	22/0	22/10	22/43					
2	22/0	4/0	37/10	22/10	37/43	22/43		
5	4/0	22/0	22/vac	37/0	22/10	22/43	37/10	37/43
8	22/0	4/0	22/vac	22/10	37/0	22/43		
16	22/0	22/vac	37/0					
mos.								
6	22/vac	22/0	"C"[c]					
8	4/0	22/0	22/vac	"C"				
12	22/vac	22/0						

a: Sample code - Temperature (°C)/ Relative humidity (%)

b: 22/vac-at 0% R.H. in vacuum sealed cans

c: "C" is commercial apple sauce

Table 5

Ranking Order for Stored Maltodextrin Preconcentrated Freeze Dried Apple Slices

	1st.	2nd.	3rd.	4th.	5th.	6th.	7th.	8th.
			Evaluated Dry					
wks.								
0	22/10[a]	22/0	22/43					
2	4/0	37/10	22/10	37/43	23/43			
5	4/0	22/10	22/0	22/vac[b]	37/0	37/10	22/43	37/43
8	4/0	22/10	22/vac	22/43				
16	22/vac	22/0	37/0					
			Evaluated Rehydrated					
wks.								
0	22/10	22/0	22/43					
2	22/10	4/0	37/10	22/43	37/43			
5	22/10	37/0	22/vac	22/10	4/0	37/10	22/43	37/43
8	4/0	22/vac	22/10	22/43				
16	22/vac	22/0	37/0					

a: Sample code - Temperature (°C) / Relative humidity (%)

b: 22/vac.- at 0% R.H. in vacuum sealed cans

Initial Significance of Difference of Organoleptic Tests for Apple Slices (0 time)

Sample	Taste: Storage Conditions	Taste: Taste Score	Taste: Significance	Texture: Storage Conditions	Texture: Taste Score	Texture: Significance	Ranking: Storage Conditions	Ranking: Taste Score	Ranking: Significance
ucrose dry	22/0	7.33	A: 0 0 / B: 0 / C	22/0	6.75	A: 0 1 / B: 1 / C	22/0	.425	A: 0 1 / B: 1 / C
	22/10	7.25		22/10	6.75		22/10	.142	
	22/43	6.92		22/43	3.67		22/43	-.567	
ucrose hydrated	22/10	7.70	A: 0 0 / B: 0 / C		—		2 22/0	.170	A: 0 0 / B: 0 / C
	22/0	7.60					22/10	.085	
	22/43	7.40					22/43	-.255	
altrin dry	22/10	7.08	A: 0 1 / B: 0 / C	22/10	6.46	A: 0 1 / B: 1 / C	22/10	.392	A: 0 1 / B: 1 / C
	22/0	6.00		22/0	6.00		22/0	.262	
	22/43	5.00		22/43	3.92		22/43	-.654	
altrin hydrated	22/10	7.08	A: 0 1 / B: 1 / C		—		22/10	.567	A: 0 1 / B: 1 / C
	22/0	7.08					22/0	.283	
	22/43	5.25					22/43	-.850	

Table 6

Significance of Difference of Organoleptic Tests for Apple Slices Stored 5 wks.

	Storage Condition	Taste Score	
sucrose dry	22/0	7.33	A
	22/10	7.33	B
	22/VAC	7.25	C
	4/0	6.75	D
	37/0	6.50	E
	22/43	6.42	F
	37/10	6.17	G
	37/43	5.67	H

Significance

	A	B	C	D	E	F	G	H
A		0	0	0	0	0	0	5
B			0	0	0	0	0	5
C				0	0	0	0	5
D					0	0	0	0
E						0	0	0
F							0	0
G								0
H								

	Storage Condition	Rank. Score	
	22/0	.513	A
	4/0	.507	B
	22/10	.387	C
	22/VAC	.246	D
	37/10	-.074	E
	22/43	-.354	F
	37/0	-.396	G
	37/43	-.828	H

Significance

	A	B	C	D	E	F	G	H
A		0	0	0	0	5	1	1
B			0	0	0	5	1	1
C				0	0	5	5	1
D					0	0	0	1
E						0	0	5
F							0	0
G								0
H								

sucrose rehydrated	4/0	8.00	A
	22/0	7.70	B
	22/VAC	7.40	C
	37/0	7.30	D
	22/10	7.10	E
	22/43	7.00	F
	37/10	6.60	G
	37/43	5.20	H

	A	B	C	D	E	F	G	H
A		0	0	0	0	0	1	1
B			0	0	0	0	5	1
C				0	0	0	0	1
D					0	0	0	1
E						0	0	1
F							0	1
G								1
H								

	4/0	.841	A
	22/0	.673	B
	22/VAC	.223	C
	37/0	.184	D
	22/10	-.051	E
	22/43	-.123	F
	37/10	-.580	G
	37/43	-1.17	H

	A	B	C	D	E	F	G	H
A		0	5	5	1	1	1	1
B			0	0	5	1	1	1
C				0	0	0	1	1
D					0	0	1	1
E						0	0	1
F							0	1
G								5
H								

Table 7

Significance of Difference of Organoleptic Tests for Apple Slices Stored 5 wks.

maltodextrin dry

Storage Condition	Taste Score		Storage Condition	Rank Score	
4/0	6.08	A	4/0	.513	A
22/0	5.85	B	22/10	.423	B
22/VAC	5.77	C	22/0	.408	C
22/10	5.77	D	22/VAC	.245	D
37/10	5.62	E	37/0	.212	E
37/0	5.46	F	37/10	.072	F
22/43	4.08	G	22/43	-.788	G
37/43	3.00	H	37/43	-1.09	H

Significance

	A	B	C	D	E	F	G	H
A		0	0	0	0	0	1	1
B			0	0	0	0	1	1
C				0	0	0	1	1
D					0	0	1	1
E						0	1	1
F							5	1
G								5
H								

Significance

	A	B	C	D	E	F	G	H
A		0	0	0	0	0	1	1
B			0	0	0	0	1	1
C				0	0	0	1	1
D					0	0	1	1
E						0	1	1
F							1	1
G								0
H								

maltodextrin rehydrated

22/0	6.79	A	22/0	.689	A
37/0	6.79	B	37/0	.474	B
22/VAC	6.64	C	22/VAC	.390	C
22/10	6.29	D	22/10	.203	D
4/0	6.21	E	4/0	.177	E
37/10	5.71	F	37/10	-.199	F
22/43	5.14	G	22/43	-.395	G
37/43	2.86	H	37/43	-1.34	H

Significance

	A	B	C	D	E	F	G	H
A		0	0	0	0	1	1	1
B			0	0	0	5	1	1
C				0	0	5	1	1
D					0	0	5	1
E						0	5	1
F							0	1
G								1
H								

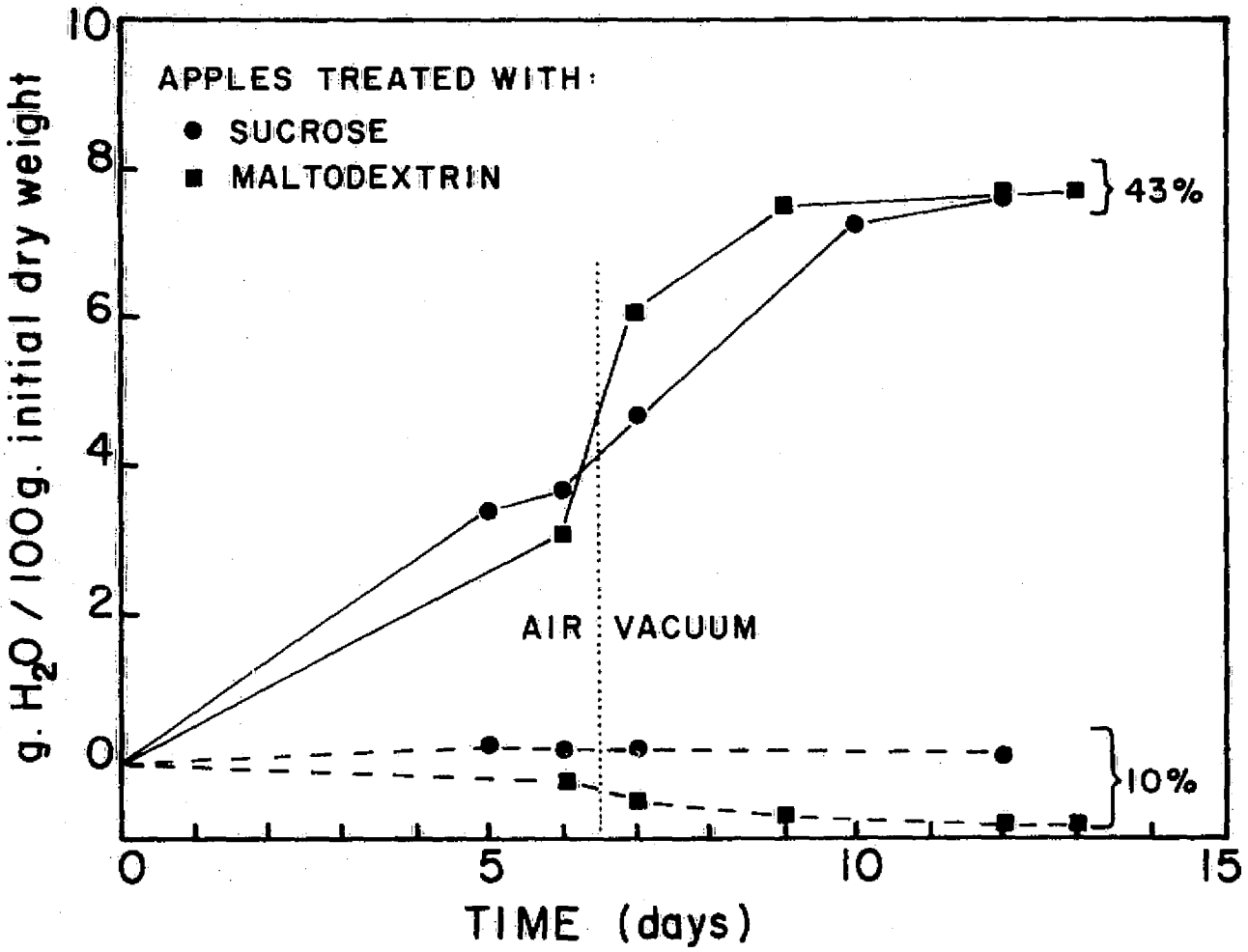
Table 8

Significance of Difference of Organoleptic Tests for Apple Slices Stored 16 wks.

Sample	Taste			Texture			Ranking		
	Storage Condition	Taste Score	Significance	Storage Condition	Taste Score	Significance	Storage Condition	Taste Score	Significance
sucrose dry	22/0	7.64	A B C A 0 0 B 0 C	22/0	7.27	A B C A 0 0 B 0 C	22/0	.348	A B C A 0 5 B 0 C
	22/VAC	7.18		22/VAC	6.82		22/VAC	-.039	
	37/0	6.91		37/0	6.64		37/0	-.309	
sucrose rehydrated	22/0	7.58	A B C A 0 5 B 0 C						A B C A 5 1 B 0 C
	22/VAC	7.00					22/0	.496	
	37/0	6.50			—		22/VAC	-.142	
							37/0	-.354	
maltodextrin dry	22/VAC	6.38	A B C A 0 0 B 0 C	22/VAC	6.85	A B C A 5 5 B 0 C	22/VAC	.131	A B C A 0 0 B 0 C
	22/0	6.08		22/0	5.77		22/0	0	
	37/0	5.46		37/0	5.77		37/0	-.131	
maltodextrin rehydrated	22/VAC	6.83	A B C A 0 1 B 1 C						A B C A 0 1 B 1 C
	22/0	6.58					22/VAC	.460	
	37/0	5.00			—		22/0	.319	
							37/0	-.779	

Table 9

List of Figures


APPLES TREATED WITH:
SUCROSE
MALTODEXTRIN
43%
10%
AIR
VACUUM
g. H2O / 100g. initial dry weight
TIME (days)
0
2
4
6
8
10
0
5
10
15

ORIGINAL PAGE IS OF POOR QUALITY

PRECEDING PAGE BLANK NOT FILMED

Name _____

Date _____

Product _____

Please evaluate these samples for flavor and texture. Taste test each one. Use the appropriate scale to show your evaluation, checking the point which best describes your feeling about taste and texture.

YOU MUST READ THIS STATEMENT AND SIGN THE FORM THAT YOU HAVE DONE SO!

1. I have notified the testers if I have any food allergies

2. I am willingly partaking in this organoleptic evaluation study. I understand that all the samples to be evaluated are composed of foods or FDA approved food grade materials. I understand that to avoid any bias in the evaluation, I may not be told the exact nature of the foods or process variations being tested, and that I have the right to withdraw at any time.

SIGNATURE _____

Code _____			Code _____			Code _____			Code _____		
Taste		Texture	Taste		Texture	Taste		Texture	Taste		Texture
	Like Extremely			Like Extremely			Like Extremely			Like Extremely	
	Like Very Much			Like Very Much			Like Very Much			Like Very Much	
	Like Moderately			Like Moderately			Like Moderately			Like Moderately	
	Like Slightly			Like Slightly			Like Slightly			Like Slightly	
	Neither Like nor Dislike			Neither Like nor Dislike			Neither Like nor Dislike			Neither Like nor Dislike	
	Dislike Slightly			Dislike Slightly			Dislike Slightly			Dislike Slightly	
	Dislike Moderately			Dislike Moderately			Dislike Moderately			Dislike Moderately	
	Dislike Very Much			Dislike Very Much			Dislike Very Much			Dislike Very Much	
	Dislike Extremely			Dislike Extremely			Dislike Extremely			Dislike Extremely	
	Reasons			Reasons			Reasons			Reasons	

FIG. 2

Name_____

Date_____

Product_____

Please rank these products according to your preference.

	Code
First	_____
Second	_____
Third	_____
Fourth	_____
Fifth	_____
Sixth	_____
Seventh	_____
Eighth	_____

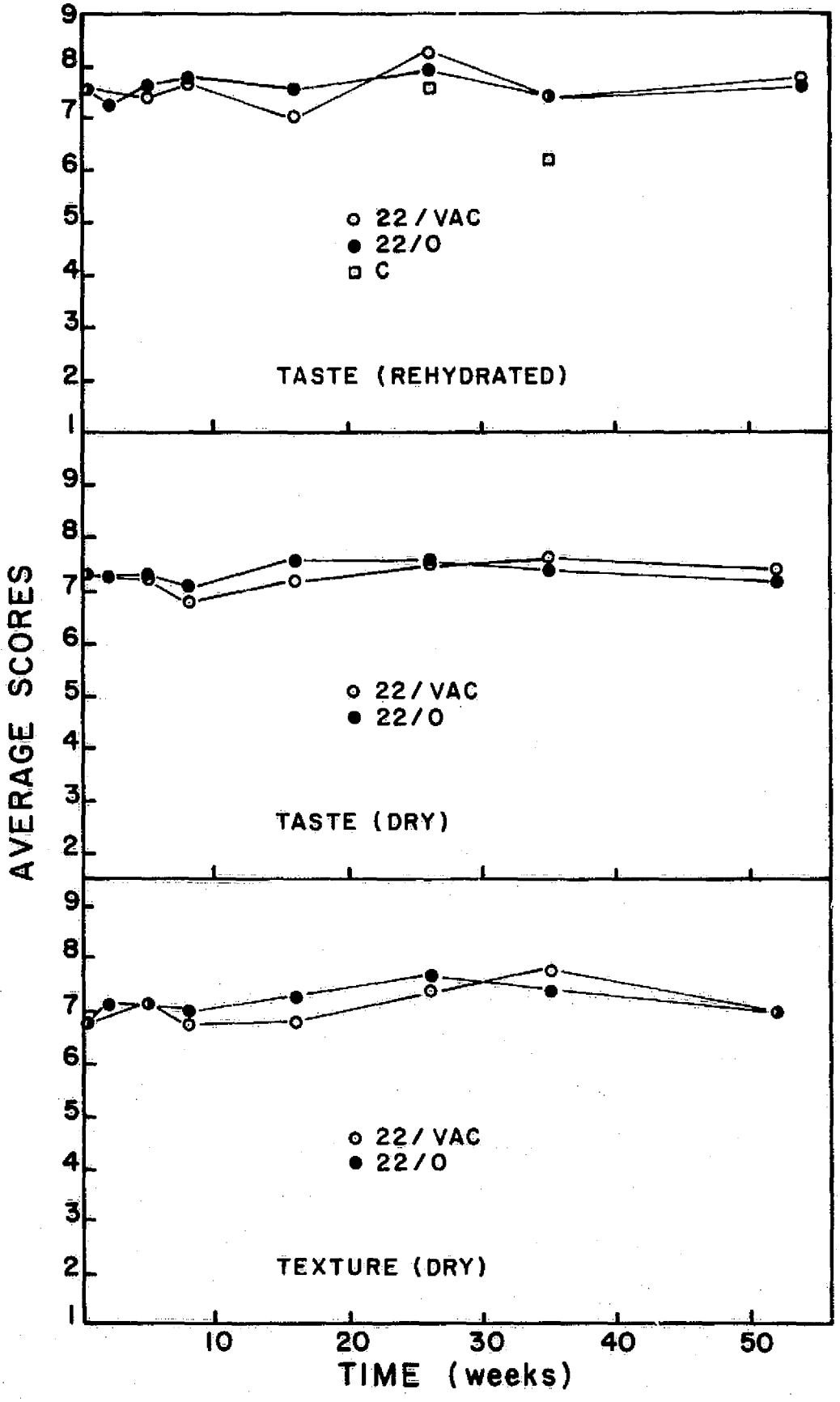
YOU MUST READ THIS STATEMENT AND SIGN THE FORM THAT YOU HAVE DONE SO.

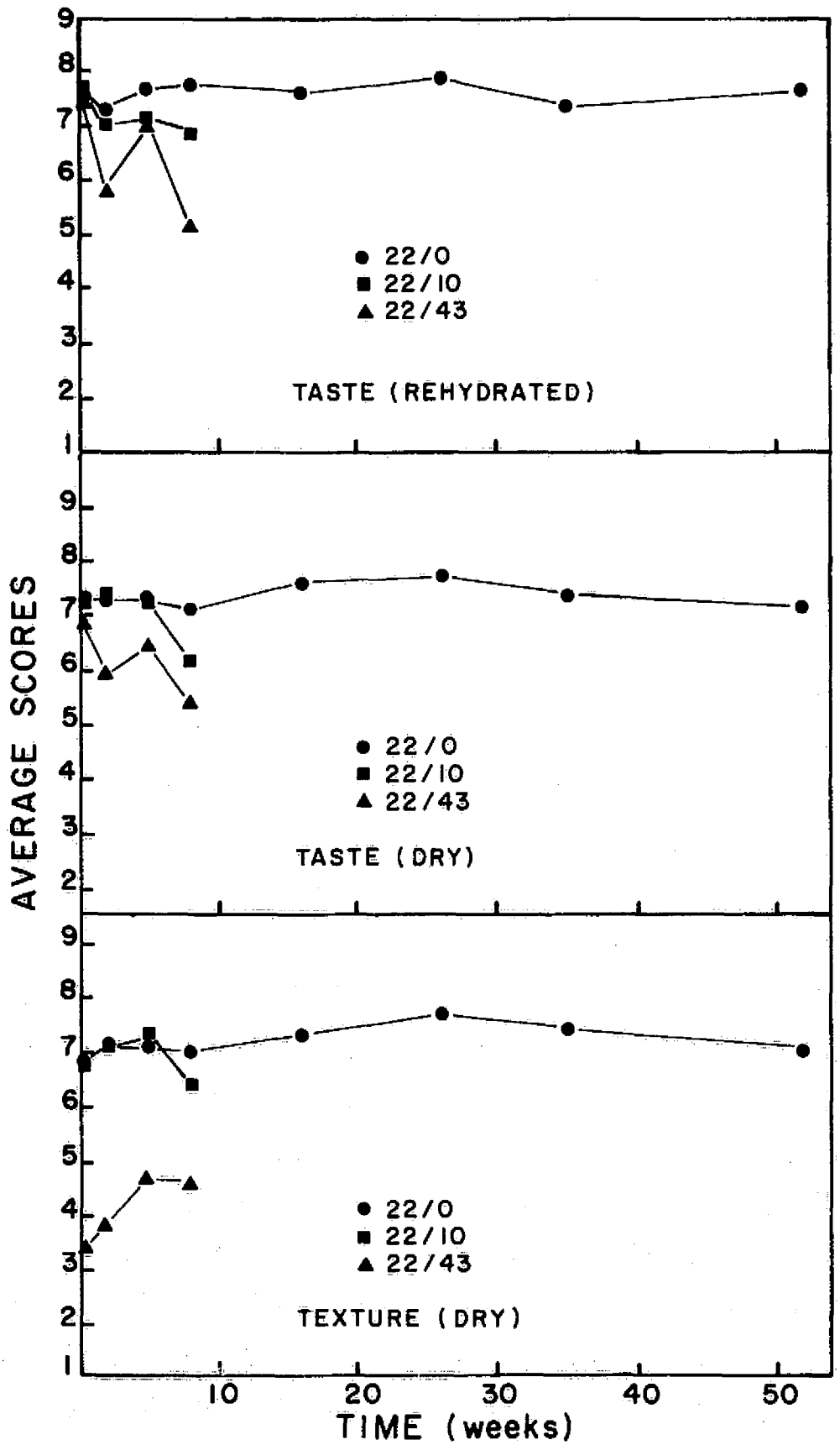
1. I have notified the testers if I have any food allergies.

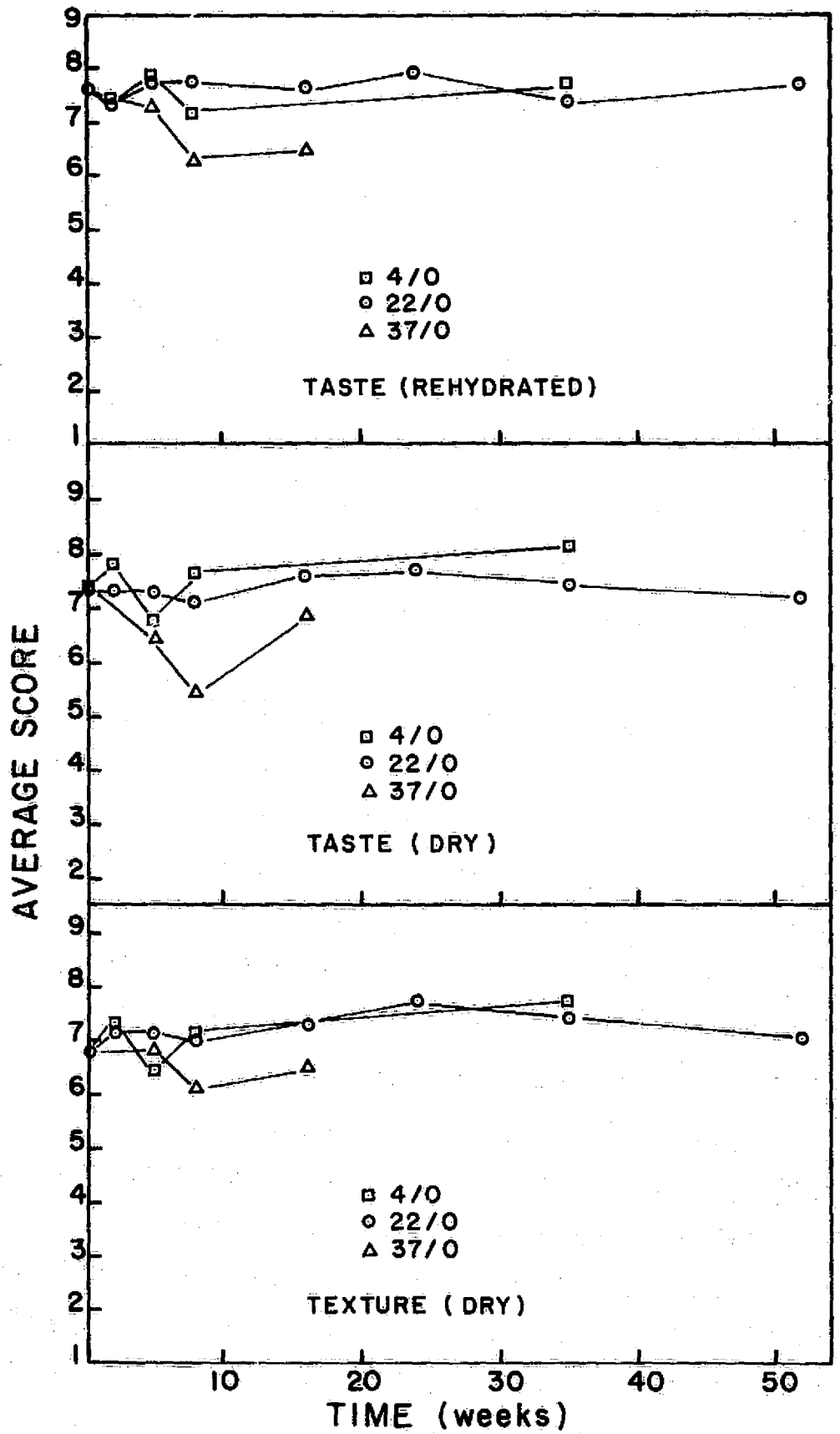
2. I am willingly partaking in this organoleptic evaluation study. I understand that all the samples to be evaluated are composed of foods or FDA approved food grade materials. I understand that to avoid any bias in the evaluation, I may not be told the exact nature of the foods or process variations being tested, and that I have the right to withdraw at any time.

SIGNATURE_____

FIG 3


AVERAGE SCORES
TASTE (REHYDRATED)
22/VAC
22/O
C
TASTE (DRY)
22/VAC
22/O
TEXTURE (DRY)
22/VAC
22/O
TIME (weeks)
10
20
30
40
50


AVERAGE SCORES
9
8
7
6
5
4
3
2
1
● 22/0
■ 22/10
▲ 22/43
TASTE (REHYDRATED)
TASTE (DRY)
TEXTURE (DRY)
10
20
30
40
50
TIME (weeks)


AVERAGE SCORE
TASTE (REHYDRATED)
TASTE (DRY)
TEXTURE (DRY)
4/0
22/0
37/0
TIME (weeks)
10
20
30
40
50

7. Summary of Results

1) Optical and electron microscope techniques were shown to give good correlation in location of surface lipid for OsO_4 stained samples.

2) Surface lipid has been shown to be associated with structural surface irregularities of the maltodextrin cake, such as ridges, bumps, depressions or the narrow spaces along or between maltodextrin platelets.

3) Quantitative determinations for surface lipid and encapsulated lipid have been developed. These are based on sequential extraction procedures the first of which extracts surface lipid, leaving the matrix unaffected. The second extraction disrupts the matrix and separates the matrix-forming material from the lipid.

4) The freezing rate and lipid phase volume was shown to influence the distribution of lipid between surface and encapsulated locations. At high phase volumes the fraction of the total lipid being encapsulated is lower, but the total amount is larger than at lower phase volumes. At these high phase volumes, also, most droplets were deformed into polygonal shapes due to the high packing density.

5) Gelatin, egg albumin and carboxymethyl cellulose were very effective in encapsulating lipid droplets. Maltodextrin was of intermediate effectiveness while glycine and Avicel were not effective.

6) Freeze dried emulsions of initially relatively uniform drop size have many larger droplets following rehydration. These large droplets come primarily from the surface deposits of lipid. The surface appears to promote coalescence.

7) The viscous flow of freeze dried carbohydrate materials was shown to be a function of material composition, moisture content and temperature. The temperature which gives viscous flow (the so-called "collapse" temperature) was shown to decrease with increasing moisture content.

8) Collapse temperatures within a single class of materials were found to be a function of average molecular weight. Mixtures of materials had a collapse temperature which was intermediate between the collapse temperatures of the components.

9) Several food grade gums were very effective at low concentrations in raising collapse temperatures. They can thus be very effective as additives for retention of structure in storage.

10) Collapse temperature increased somewhat as the initial solute concentration of a given material was increased. Freezing rate also had a small effect.

11) Lipid was incorporated into the artificial food matrices as small droplets without loss of texture. β-carotene could be dissolved in the lipid phase and in this way added to the AFM.

12) Vitamin C was added to the AFM in both lipid-soluble forms (as in 11 above) and in water-soluble form by adding ascorbic acid to the gel and to the crosslinking solution.

13) Static and dynamic compression tests have shown that the calcium alginate is the major contributor to the texture of the crosslinked system. The non-crosslinked material is found to be very weak.

14) Gelatin, pectin and sucrose act to modify the texture and mechanical properties of the basic calcium alginate gel. Gelatin tends to give a stronger gel, while the presence of pectin or sucrose give a weakening action.

15) The strengthening properties of gelatin on the calcium alginate gel were lost when tests were conducted at 200°F, and restored when the samples were re-tested at room temperature.

16) The mechanical properties of the AFM do not model <u>any one particular</u> fruit or vegetable tested, but rather individual properties are similar to the properties of different fruits. All properties are in the range of values determined for a variety of fruits and vegetables.

17) Osmotic preconcentration of fruit slices with sucrose prior to freeze drying has been shown to give products with superior quality.

18) The osmosis process can be analyzed as an unsteady state diffusion process with the change of a normalized % total solids content as the concentration term. Analyses yield osmosis rates and mass transport factors which can be used to compare the effectiveness of various solutes and process variables.

19) Mass Transport Factors increase with increase in solute concentration. The increase is not solely due to higher absolute solute concentrations since correcting the mass transport factors for concentration results in mass transport coefficients which are still a function of concentration.

20) Gentle agitation had an effect on osmosis kinetics only at the highest solute concentrations (60% solids).

21) Apple slices pick up solute from the osmosis solution. The amount of solute picked up increased with increase of osmosis solution concentration and was only slightly dependent on the solute.

22) Lactose, Sucrose and Maltodextrin were essentially ineffective at 25% solids. Salt at that concentration was a very effective osmosis solute.

23) Mixed solute systems with sucrose as one component were effective as osmosis solutes. With agitated systems the rates were about half that of pure sucrose at the same total concentration. Without agitation, there were essentially no differences. Organoleptic properties of mixed systems differed from pure sucrose in that they gave products of lower sweetness levels.

24) Mixing apple slices with equal weights of dry lactose: sucrose blends gave concentrated products of good quality. The replacement of sucrose with lactose gave reduced effectiveness, though satisfactory levels of concentration were accomplished with up to 75% of the sucrose having been replaced by lactose.

25) High quality of Sucrose preconcentrated freeze dried apple slices was maintained for 1 year of storage at room temperature, provided that the product was maintained dry.

26) Moisture uptake was the most critical factor affecting storage stability. Elevated temperature (37°C) resulted in a slight reduction of organoleptic quality of dry slices. The combination of elevated temperature and moisture content was most detrimental, rapidly giving an unacceptable product.

27) Packaging with air or vacuum in the headspace had no effect on the storage stability for dry product at 22°C.

28) Trends of storage behavior were similar for samples concentrated with sucrose or maltodextrin. Sucrose samples, however, always had higher organoleptic test scores, though with desirable storage conditions (i.e. maintain dry at 22°C or below) both freeze dried apple slices were highly acceptable.